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M.Sc. THESIS.

THE OXIDATION OF NATURAL GAS AND METHANE WITH GASEOUS OXYGEN UNDER HIGH PRESSURES AND AT HIGH TEMPERATURES.

By

Victor Thomas, B.Sc.

Dept. of Chemistry. April, 1936.

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THESIS

THE OXIDATION OF NATURAL GAS AND METHANE WITH GASEOUS OXYGEN UNDER HIGH PRESSURES AND AT HIGH TEMPERATURES:

Submitted in Partial Fulfilment of the
Requirements for the Degree of Master
of Science.

By

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INTRODUCTION.

Gaseous paraffins of low molecular weight are available in tremendous quantities and they are continuing to attract the attention of the chemist as potential raw materials for the manufacture of a great variety of chemical products. They are available in large quantities in natural gas and are also produced in quantity in oil refining processes and in the carbonization of coal.

Commonly there are satisfactory markets for any one of these gases as fuels. However, in some regions where the supplies are very great and the market small, a great waste may occur. This applies especially to the province of Alberta. Wastage has reached in past years as much as 6×10^8 cubic feet per day. The Turner Valley field in the province of Alberta at present produces 2.5×10^8 cubic feet per day of which about 10 percent is usefully employed. In addition a few million feet of stabilizer gas of high value are wasted. This gas consists chiefly of ethane, propane and butane. The field at present for all practical purposes, is running wide open. To-day the reserves in the field are greatly depleted, probably between $3\text{-}5 \times 10^{10}$ cubic feet remaining down to a pressure at which it could be economically extracted. There does not appear to be any

possibility in the near future of using this gas in the logical way as fuel. The possibility of chemical conversion to useful liquid products of high value and ease of transportation offer a field of inquiry. Regardless of the future of Turner Valley the province of Alberta has available in addition a possible gas production estimated at 4 x 10^8 cubic feet daily, which being dry gas is not being removed wastefully.

The gaseous hydrocarbons are, as a rule, very resistant to chemical reactions. They are generally stable and only attacked under drastic conditions. However, their reactions, with only one important exception, are highly exothermic and also involve large decreases in free energy. The combination of drastic treatment required to initiate the reaction and large energy decreases associated with the reaction makes the problem of control very difficult. Control of velocity and extent of the reaction is, nevertheless, essential. Of the series of reactions a hydrocarbon can undergo with another reagent, the primary reaction is usually the most important in producing a useful liquid or gaseous product while the secondary reactions leading to the greatest decreases in free energy give products of little or no economic value.

The most promising reactions of hydrocarbons

from the point of view of economic investigations may be classified as follows:-

1. Pyrolysis
2. Halogenation
3. Oxidation

Pyrolysis of the lower homologues of the gaseous hydrocarbons requires high temperatures. However as the molecular weight increases, cracking takes place at successively lower temperatures. Methane can be cracked either by heating it externally or having the necessary heat applied internally by partial combustion. The ultimate products formed are carbon black and hydrogen or water. Controlled pyrolysis will yield olefines, acetylene and aromatics to the extent of 12 percent or so of the methane. The process is not economical however although it is used under certain conditions as a source of hydrogen. The aromatics are a by-product. The higher homologues of the gaseous paraffins may be pyrolyzed readily to form olefines as one of the main products. These olefines can be polymerized either simultaneously or separately to produce naphthenes, aromatics and other higher molecular weight hydrocarbons. The largest percentage of the unsaturates are at present polymerized to produce motor fuels and low boiling point hydrocarbon fractions which are used as solvents in the chemical

industries.

The chlorination of the lower homologues of the gaseous paraffins has in recent years received much attention. The chlorination of methane to produce the mono-chloro derivative and its subsequent hydrolysis to methyl alcohol shows promise. However, a great difficulty appears in limiting the reaction to one hydrogen atom alone. Bromination and fluoration have not been investigated a great deal, due no doubt to the fact that the initial cost of the materials are of necessity very high. Various chlorinated derivatives of pentane have been made on a commercial scale. The interest here lies in the fact that higher alcohols can be produced which are eventually transformed into solvents for cellulose acetate. The mono-chloro derivatives are also used as raw materials in the manufacture of fatty acids, drying oils and other similar materials.

Oxidation is a promising reaction in view of the number of reactions possible and the variety of useful products such as alcohols, aldehydes, acids and resins that may be produced.

Attempts have been made to oxidize methane selectively to carbon monoxide and hydrogen. The process is simple requiring only a limited supply of oxygen, a high temperature, and a metallic catalyst. More satisfactor

results have been obtained using steam over a nickel catalyst. The carbon monoxide and hydrogen mixture is used in the production of synthetic methanol. Further the carbon monoxide may be oxidized by means of more steam and a suitable catalyst to carbon dioxide, its subsequent removal by well known processes leaving pure hydrogen. The above two-stage process to produce hydrogen is used in the manufacture of ammonia and in the high pressure hydrogenation of petroleum products.

In recent years, the direct oxidation of the lower gaseous paraffins with oxygen or air has been investigated for the production of any one particular product to a greater or less extent by careful control of certain variables, such as for example, temperature and pressure. Methyl alcohol has been isolated in large quantities in the direct oxidation of methane. The nature of the reaction is such that control is obtained only by the use of elevated pressures. Oxidation at atmospheric pressure results in low yields of useful products and high yields of carbon oxides and water.

This present investigation is a continuation of the one(9) carried out a few years ago on the direct oxidation of natural gas in the presence of various catalysts. A new apparatus has been designed whereby better control of the oxidation reaction may be obtained and an investigation

of the variables concerned readily carried out. The effect of such variables as pressure, space velocity, composition and catalysts were investigated in the direct oxidation of natural gas and methane with gaseous oxygen.

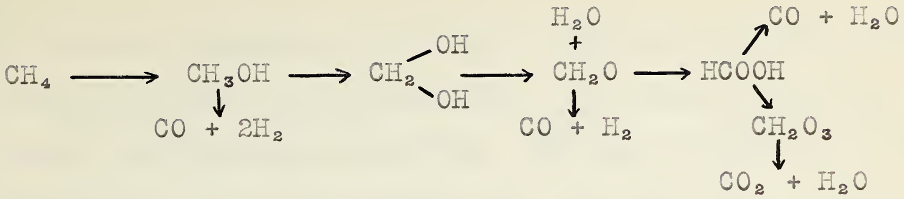
Apart from the primary purpose of the research, the production of useful liquid products, considerable information regarding the mechanism of oxidation of hydrocarbons has been obtained. The universal importance of fuels and the processes of combustion makes such information of value on this account alone.

LITERATURE REVIEW:

The earlier workers (23) on the oxidation of methane assumed that carbon monoxide and water were the initial products, hydrogen being preferentially attacked by oxygen. Kersten (20) came to the conclusion that carbon monoxide and hydrogen were the primary products and if carbon was formed first it burned preferentially to carbon monoxide before the hydrogen reacted. Misterli (24) put forward the same idea, namely, that the preferential combustion of carbon was the first step. Armstrong (2) suggested that the oxygen molecule combined with the hydrocarbon to form a dihydroxy derivative and that water could react with the complex to form hydrogen peroxide. However, he had no experimental evidence to support his suggestion.

The greater part of the work on the combustion of the lower paraffins at atmospheric pressure was done by Bone (3) and his collaborators. From the result of their imvestigations they put forward the *Hydroxylation* theory to explain the formation of the various oxidation products. The *Hydroxylation* theory postulated the successive formation of hydroxylated compounds each of which could gain additional hydroxyl groups or lose water and break down in one or more ways .

According to the *Hydroxylation* theory methane would be oxidized through the following stages:-



The final products being carbon monoxide, carbon dioxide and water.

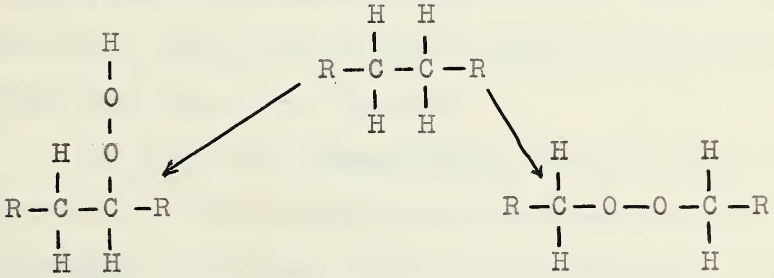
Evidence for the Hydroxylation theory was meagre at that time since the mono-and di-hydroxy derivatives could not be isolated. Bone and Drugman (3) reported water and formaldehyde among the first oxidation products of methane below its ignition point. No trace of methanol was found.

A characteristic of all direct oxidation experiments on methane and other gaseous hydrocarbons was the production of aldehydes. Certain investigators concluded that another compound was formed before the aldehyde and they assumed that a form of peroxide was built up between the oxygen molecule and the hydrocarbon. Because of this the Peroxide theory was born in direct opposition to the Hydroxylation theory.

The Peroxide theory was forcasted by Harries (18) who showed that in the reaction between ozone and a paraffin a labile peroxide was formed. However, the theory as it stands to-day was developed from the great amount of work done on the oxidation of liquid paraffins

to explain knocking in internal combustion engines. The theory is based upon experiments with liquid paraffins rather than gaseous paraffins. The main workers in this particular field being Callendar (11) and Brunner and Rideal(10).

According to the Peroxide theory a paraffin was oxidized as follows:-



alkyl hydrogen peroxide dialkyl peroxide

with the formation of an alkyl hydrogen peroxide or a dialkyl peroxide. These peroxides could in turn break down to form water, aldehydes, acids and other similar compounds. The presence of a peroxide in most of the oxidations carried out on the lower paraffins could not be detected and hence the Peroxide theory has been greatly criticized.

Egerton (13) does not believe in the initial formation of a stable peroxide. He assumes the formation of a temporary peroxide which can rearrange to form a stable peroxide or decompose into another secondary product. Further criticism of the Peroxide theory was

furnished by Pope, Dykstra and Edgar (28) who worked on the vapor phase oxidation of the isomeric octanes. The early formation of aldehyde and water in the reaction products and their presence under all conditions led them to assume that the aldehyde was the primary oxidation product. The aldehyde was assumed to decompose further to aldehydes of lower molecular weight, carbon dioxide and water. With insufficient oxygen carbon monoxide was formed besides carbon dioxide.

Since the Hydroxylation theory explained the formation of the various oxidation products more satisfactorily,it was in most cases accepted in preference to the Peroxide theory. More recent work to be discussed later offers confirmation of this theory.

Bone and Wheeler (4) showed that when methane-oxygen mixtures at atmospheric pressures were circulated through a tube containing pieces of porous porcelain maintained at temperatures of 500-600 °C. formaldehyde was formed in quantities equal to 15-20 % of the methane burned. Small amounts of formic acid were also obtained but the presence of methyl alcohol, the assumed primary oxidation product could not be detected. The static experiments with methane at atmospheric pressures yielded similar results.

It was not until suitable gaseous oxidation

catlysts were used that alcohols in measurable quantities were obtained from their corresponding hydrocarbons.

Layng and Soukup (21) obtained small quantities of methanol by oxidizing methane in the presence of oxides of nitrogen. They investigated the catalytic partial oxidation of various mixtures of methane and ethane with oxygen in a dynamic system at temperatures 100-700 °C. Catalysts such as copper and silver, oxides of metals, and barium oxide did not prove very satisfactory from the standpoint of carbon conversion to useful products. Small amounts of nitrogen oxide were found to promote the oxidation reaction. Auxiliary catalysts used with nitrogen oxide appeared to have little effect on the oxidation. However, methyl nitrite was shown to have a slight promoting action on the partial oxidation of the hydrocarbons.

Later Bibb and Lucas (8) obtained good yields of formaldehyde in the partial oxidation of natural gas by air, using nitric acid as the catalyst. Under some conditions a 4% conversion of the hydrocarbon to aldehyde was realized, while under other conditions a condensate containing 25% of formaldehyde was obtained. For satisfactory yields of formaldehyde the time of contact of the gases in the furnace at 700-750 °C. should be less than 0.5 seconds. The presence of formaldehyde in the condensate

suggested that the oxidation followed the steps postulated by the Hydroxylation theory.

None of the oxidation processes using solid catalysts at atmospheric pressure have up to the present time given large yields of the initial hydroxylated compound. Cristesco (12) has reported a process at atmospheric pressure and relatively low temperatures giving large yields of methanol by the oxidation of methane. Essentially the procedure consisted of bubbling various gas mixtures at atmospheric pressure through boiling water containing submerged catalysts. The liquid from this process was then fractionally distilled to separate the alcohols, the uncondensed gases being sent through scrubbers to remove the aldehydes. Yields as high as 57% are reported upon passing a mixture containing three parts of air and one part of methane through the apparatus containing lead oxide with copper oxide as a supplementary catalyst. By using a mixture of carbon monoxide and hydrogen good yields of ethyl alcohol were obtained under the proper conditions. The results reported are attractive. Efforts were made here to duplicate these experiments without any success whatever.

Generally speaking, oxidation of methane at atmospheric pressure has not resulted in yields of methanol or formaldehyde of commercial interest. Such

work, however, has clarified greatly the mechanism of the process of combustion.

In recent years a considerable amount of work has been carried out on the explosive combustion of methane under pressure and to a lesser extent on the slow controlled combustion under pressure. The use of pressure offers an obvious means of raising the yield of the primary oxidation products at the expense of the gaseous products. On the basis of the Hydroxylation theory the over all reactions of importance in yielding useful products may be given as follows:-

1. $2CH_4 + O_2 \longrightarrow 2CH_3OH$
2. $2CH_3OH + O_2 \longrightarrow 2CH_2O + 2H_2O$
3. $2CH_2O + O_2 \longrightarrow 2HCOOH$.

On the basis of Le Chatelier's principle, an increase in pressure should increase the survival of the alcohol and formic acid at the expense of the formaldehyde. The end reaction to carbon oxides, hydrogen and water are either unaffected or opposed by increased pressure. Because of this and also to obtain a better insight into the oxidation mechanism of the paraffins work at high pressures was initiated.

The explosive combustion of methane has received considerable attention from Bone (7) with the object of determining the mechanism of combustion. The first work

reported with the production of methanol by controlled slow oxidation is that of Yoshikawa (32). He carried out a series of experiments using a flow method within the pressure range 12-100 atmospheres, with a gas mixture of methane and air in the ratio of 1:1, 2:1, 3:1. A decided reaction was noted in the range of pressures used at temperatures 300-400 °C. The main products obtained were carbon monoxide, carbon dioxide, water, methyl alcohol and formaldehyde. An increase in pressure was found to favour the survival of the alcohol. The reaction was promoted by a little nitric acid vapour at 350 °C.

Newitt and Haffner (25) using a static method have been able to obtain small yields of methanol. In their work an 8.1 : 1 methane-oxygen mixture was allowed to react in a steel chamber of 500 cc. capacity at different temperatures and initial pressures. The effect of increasing the pressure from 48.2-150 atmospheres was to increase, (1) the rate of reaction for any given temperature, (2) the amount of methanol and formaldehyde in the product, (3) the ratio of methanol to formaldehyde in the product. The amount of oxides of carbon represented as much as 70% of the methane that had reacted. An increase in pressure was shown to confirm qualitatively the results as predicted by Le Chatelier's principle and confirmed the Hydroxylation theory.

Pechler and Reder (29) in order to confirm the qualitative results of Newitt and Haffner carried out a series of flow experiments at 100 atmospheres pressure. At this particular pressure a number of runs were made at 500 °C. using different concentrations of oxygen. The results of their experiments showed that higher temperatures were needed than in the case of the static bomb experiments, but that better yields were obtained at comparable pressures The conversion to alcohol increased with decrease in inlet oxygen concentration until at 0.6% inlet oxygen about 60% of the oxygen appeared in the alcohol. Yields of alcohol based on the total carbon burned were as high as 22.3%.

Up to this time no complete systematic investigation of the variables concerned in the high pressure oxidation of the paraffins had been carried out. Consequently,Newitt and Szego (26) carried out an investigation with the object of finding the order of formation of the various oxidation products and the optimum conditions for their survival. A flow method was used and the temperature, pressure, rate of flow and oxygen concentration so adjusted as to obtain an optimum survival of the useful oxidation products. Pressures up to 50 atmospheres were used and temperatures within the range 290-340 °C. The following table shows the summarized results for the oxidation of methane at 50 atmospheres pressure.

% O_2 in medium	Temp. °C.	% CH_4 burned surviving as CH_3OH	 CH_2O
60.0	370	13.7	0.8
5.0	410	29.0	1.4
3.0	430	51.0	4.1

A similar set of results was obtained for the oxidation of ethane at 50 atmospheres pressure.

% O_2 in medium	Temp.°C.	% C_2H_6 burned surviving as C_2H_5OH	 CH_3CHO	 CH_3OH	 CH_3COOH
9.9	290	23.9	4.9	16.0	2.9
5.0	305	32.1	4.1	2.2	2.4
3.0	360	63.2	4.8	trace	1.1

By diminishing the inlet oxygen concentration the survival of the alcohol was raised to over 50% of the methane burned and over 60% of the ethane burned. No unsaturates or peroxides were formed in any of the runs.

These experiments and those of other investigators emphasized the fact that a low oxygen concentration was essential for a high survival of the useful oxidation products.

An investigation, preliminary to the present one, was carried out by Broughton(9) on the effect of solid catalysts on the reactions. He used a flow method and a mixture of 7.5% oxygen in Viking natural gas. Metallic catalysts were found to be efficient while oxides of polyvalent metals such as vanadium and tungsten, useful in other oxidation reactions, were found to be of no

catalytic value. To obtain satisfactory yields it was found desirable to work at pressures around 200 atmospheres and at temperatures within the range 300-350°C.

Wiezevitch and Frolich (31) carried out an investigation on the oxidation of various paraffins using a flow apparatus. Preliminary runs were made on methane, ethane, and a natural gas containing 86.6% methane with small amounts of ethane and propane. Oxygen was used as the oxidizing medium although air was found to give the same results provided that the pressure was increased to correct for the diluting effect of the nitrogen. Metallic catalysts such as calcium, chromel, silver and aluminum were found to give better results than empty tubes. An increase in space velocity was found to increase the production of desirable products without altering the oxygen efficiency or carbon conversion to useful products. Increasing the temperature of operation from 300-500 °C. tended to produce more carbon monoxide and carbon dioxide, at the expense of the other useful products. The maximum operating temperature at 135 atmospheres pressure for methane and ethane was 370 and 500 °C. respectively. A few runs made on natural gas showed that methyl alcohol could be isolated in quantities three to eight times the amount of formaldehyde. In order to insure that the products did not come from the oxidation of the

methane, experiments were carried out on pure methane under the same conditions. The results obtained showed that the operating temperature was below the ignition point of the methane. However, in some of the runs the amount of methyl alcohol formed could not be accounted for if all the ethane reacted quantitatively to produce the primary oxidation product. This suggests that in the presence of the ethane some of the methane reacted.

With natural gas at 135 atmospheres pressure, 5.4% inlet oxygen concentration and a temperature of 390°C. a product containing 30.3% methyl alcohol, 3.3% formaldehyde and 0.5% formic acid was obtained. One cubic meter of the natural gas yielded 0.0615 litres of alcohol with small quantities of formaldehyde and formic acid. The total amount of useful oxidation products corresponded to 16.2% of the inlet oxygen and 3.7% of the total ingoing carbon.

This work showed that yields were only high if the oxygen concentration was low and suggests that any commercial process will have to be circulatory in nature. The unoxidized hydrocarbon will be separated from the liquid products, oxygen added, and the mixture passed through the reactor again.

No theory up to the present has been able to explain the mechanism of combustion of paraffins at high

and low pressures. The Hydroxylation theory has explained fairly satisfactorily the analytical but not the kinetic data. Recently, Norrish (27) has put forward a theory to explain all the facts now at hand on the combustion of the hydrocarbons. While the Hydroxylation theory is satisfactory from the point of view of explaining the origin of the products, it can be criticized for the kinetics of the reactions.

Norrish disagrees with the Hydroxylation theory as to the origin of formaldehyde in the oxidation of methane. He regards the formaldehyde as the primary product while the alcohol is only formed under special conditions. His theory is based upon the existence of free radicles or molecular fragments which are produced when hydrocarbons are heated to high temperatures. The use of free radicles in explaining the mechanism of a reaction is generally accepted as justified and is usually used. The production of free radicles and a mechanism involving a chain reaction has been suggested by Norrish for the oxidation of methane. He assumes as primary reactions,

$$O + CH_4 \longrightarrow CH_2: + H_2O$$

$$CH_2: + O_2 \longrightarrow CH_2O + O$$

and so on. The chain can be terminated by either of two ways,

$$O + CH_4 + X' \longrightarrow CH_3OH + X$$

$$O + \text{surface} \longrightarrow 1/2\ O_2$$

where X' stands for a hydrocarbon molecule having the necessary energy of activation.

From the above equations it is seen that an increase in pressure favors the survival of the alcohol since a ternary collision must take place before its formation. A reasonable explanation of the predominance of aldehydes at low pressures and of methanol at high pressures is given by the theory. Norrish also claims a satisfactory interpretation of the kinetic data on oxidations.

The literature records many patented processes on natural gas. On the whole, the literature on the oxidation of the lower paraffins is scanty and no comprehensive investigation covering all controlling factors has yet appeared. The present work is an attempt in this direction.

EXPERIMENTAL METHODS.

Materials.

Natural gas from the Viking field was used in the preliminary work. On analysis in a modified type of Bureau of Mines gas analysis apparatus it showed the following composition.

CH_4 - 90.79 %

C_2H_6 - 3.50 %

N_2 - 5.71 %

Higher hydrocarbons such as propane were present in small amounts and are included in the ethane figure. Since the natural gas was odorized with mercaptans and alkyl disulfides it was necessary to purify it before use. The method of purification will be described in a later section.

In the later experiments Cracked gas was used. This gas was prepared from Viking natural gas by removing the heavier hydrocarbons by pyrolysis. A series of experiments based upon previous work (17) showed that pyrolysis at a temperature near 780 °C. and the proper rate of flow resulted in the decomposition of all hydrocarbons in the gas except methane. The products of pyrolysis were removed in a very simple manner to be described later. The Cracked gas which will be called Methane hereafter showed the following average analysis:-

CH_4 - 94.3 %

N_2 - 5.6 %

Impurities (C_2H_4, H_2) - 0.1 %

The catalysts used in this investigation were copper, glass, enduro steel and silver. The copper catalyst was used in small pieces 3/16'' square and 3/32'' thick which were cut from a copper gasket ring. The weight of the copper used was 39.8 gms. with a total volume of 4.46 cc. Prior to being used it was activated by alternate oxidation and reduction at 350 °C. Air was used as the oxidizing medium while hydrogen and methyl alcohol vapours were used as the reducing agent. In the earlier experiments on natural gas the copper catalyst was poisoned frequently and this necessitated its removal from the reactor to be cleaned. It was found by experience that if the copper catalyst was cleaned with dilute nitric acid rather than by activating by the above mentioned method the yields were not changed. Consequently in later experiments the copper catalyst was always cleaned, in case of poisoning, with dilute nitric acid to bring back its former activity.

The glass used was obtained from a 1/8'' diameter soft glass tubing which was cut into lengths of approximately 3/8''. The total weight of the glass used was 8.16 gms.

Enduro steel was used in the form of machine turnings. These were thoroughly washed with ether to remove any oil or grease. The total weight of the

turnings used was 17.13 gms. with a total volume of 2.20 cc.

Silver was used in 3/16'' squares which were cut from a silver sheet 0.0004'' thick. The surface was cleaned with warm dilute nitric acid and washed thoroughly with distilled water. The total weight of the silver catalyst used was 15.35 gms. with a volume of 1.46 cc.

Apparatus.

The pyrolysis apparatus is shown in Figures 1 and 2. The process consisted essentially of cracking the higher hydrocarbons and odorant sulphur compounds and then removing the undesired products of the reactions.

The flow of gas was controlled by observing the flowmeter ,A, and manipulating the inlet stopcock. The gas was passed through a calcium chloride drier ,B, to a 0.75'' quartz tube ,C, heated to 780 °C. over a length of 12 inches, in which conversion of the ethane, heavier hydrocarbons and sulphur compounds in the natural gas to liquids, methane, olefines, hydrogen, and hydrogen sulfide occurred. The gas was then passed through a glass wool filter ,D, to remove most of the tar, through a soda-lime tower ,E, to remove sulphur compounds and to an activated charcoal absorber ,F, which removed to a great extent the heavier hydrocarbons. The gas was next scrubbed by sulphuric acid in the tower ,G, holding about 400 cc. concentrated sulphuric acid containing about 1% silver sulphate as catalyst. The acid was heated to 70 °C. with a gas burner. Continuous circulation of hot sulphuric acid was obtained by the glass and mercury pump ,G, as shown. This scrubber removed the olefines completely. The sodium hydroxide scrubber ,H, removed any sulphur dioxide produced by the reduction of the sulphuric acid and

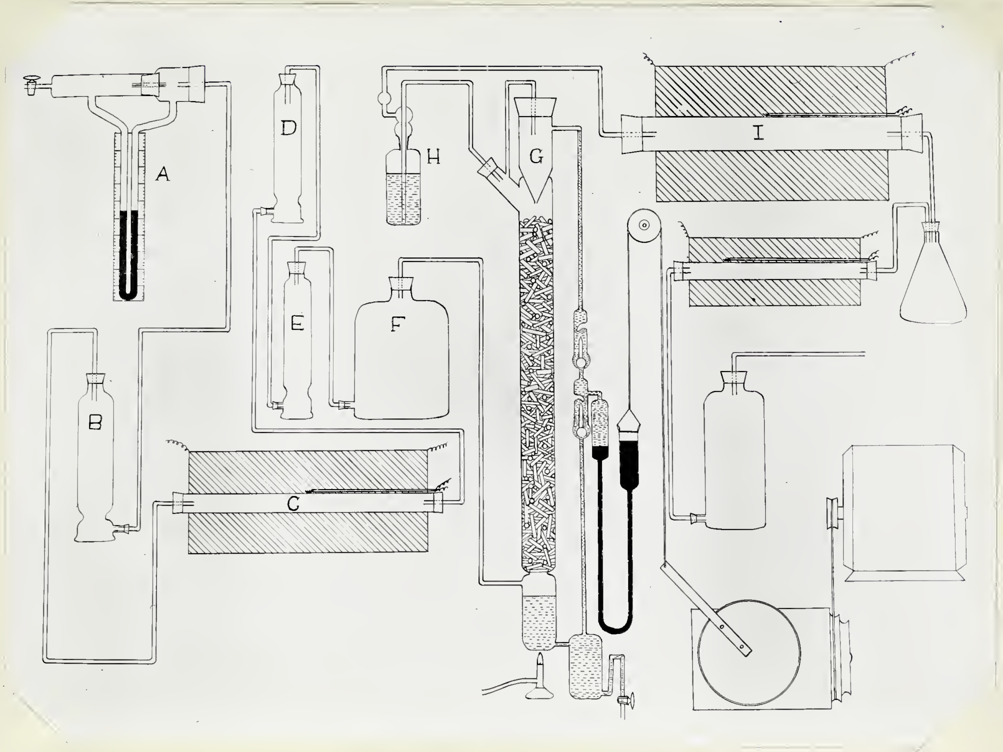


Figure 1.

Pyrolysis Apparatus.

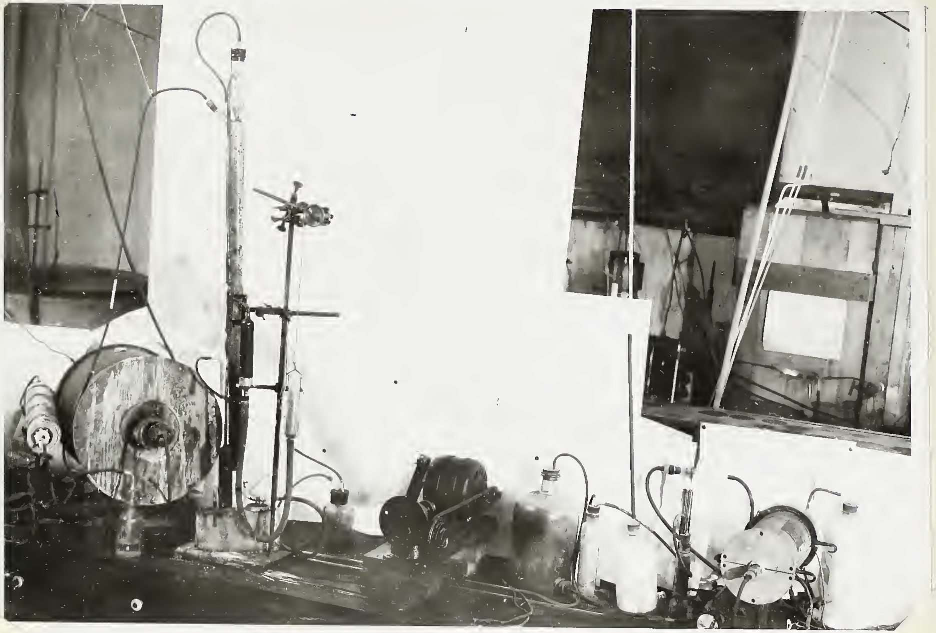


Figure 2.

Pyrolysis Apparatus.

oxidation of the sulphur compounds. The gas was then passed over 2 killograms of copper oxide ,I, at 400 °C. which oxidized the hydrogen, carbon monoxide and any traces of unsaturates left to carbon dioxide and water. The bulk of the water produced was retained in the water trap, after which the gas was led through a smaller copper oxide tube at the same temperature to remove the last traces of hydrogen. A soda-lime tower removed the carbon dioxide produced over the copper oxide. By varying the rate of flow and temperature to give the optimum conditions it was possible to prepare 40 cubic feet of gas per day. The composition of the gas was 94.5 ± 0.5 % methane, 5.3 ± 0.5% nitrogen with 0.2 % or less of other gases chiefly hydrogen. The variable amount of methane was produced from the ethane due to slight variations in the temperature of the pyrolysis tube. The consumption of chemicals per 100 cubic feet of gas prepared was 1000 cc. technical grade sulphuric acid, 50 gms. calcium chloride, 50 gms. activated charcoal and 80 gms. soda-lime. The charcoal was re-activated when saturated by distillation with super-heated steam at 300 °C. fo 20 minutes. All temperatures were measured with thermocouples and were held constant to 5 ° of the desired temperature, by manual control of the heating current through the rheostats. The purified gas was stored in water-sealed gas holders from which it was pumped into the high pressure

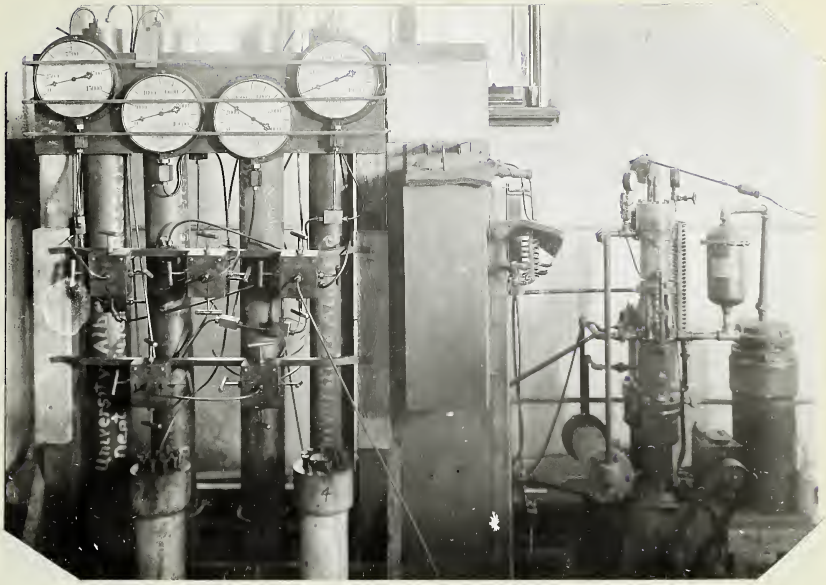

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Figure 3.

Compressor and Gas Storage System.

The Rix three stage compressor is shown in the right background, and the storage cylinders in the left foreground.

storage system (Figure 3).

Two high pressure systems were used in this work, one with natural gas-air mixtures and the other with methane-air mixtures.

In the experiments with natural gas-air mixtures a relatively simple procedure was possible. Partially dried air was stored under operating pressure in storage tanks of such capacity that during the course of an experiment the pressure drop would be relatively small, 50 lbs. or so. Natural gas was stored similarly but at a pressure some 500 lbs. smaller than that of the air. The air was passed through a steel tube containing solid potassium hydroxide to remove traces of water and carbon dioxide before being admitted through the control valve to the reacting system. A check valve in this line offered some safeguard against the accidental entry of gas from the reacting system to the air storage. The natural gas was passed first through 93 % sulphuric acid contained in a steel bottle to remove or destroy odorant sulphur compounds in the gas, then through a tube containing solid potassium hydroxide to remove sulphur dioxide produced in the acid bottle and finally through absorbent charcoal to remove traces of impurities. From the charcoal tube, the gas was led through a check valve to the control valve leading to the reacting system.

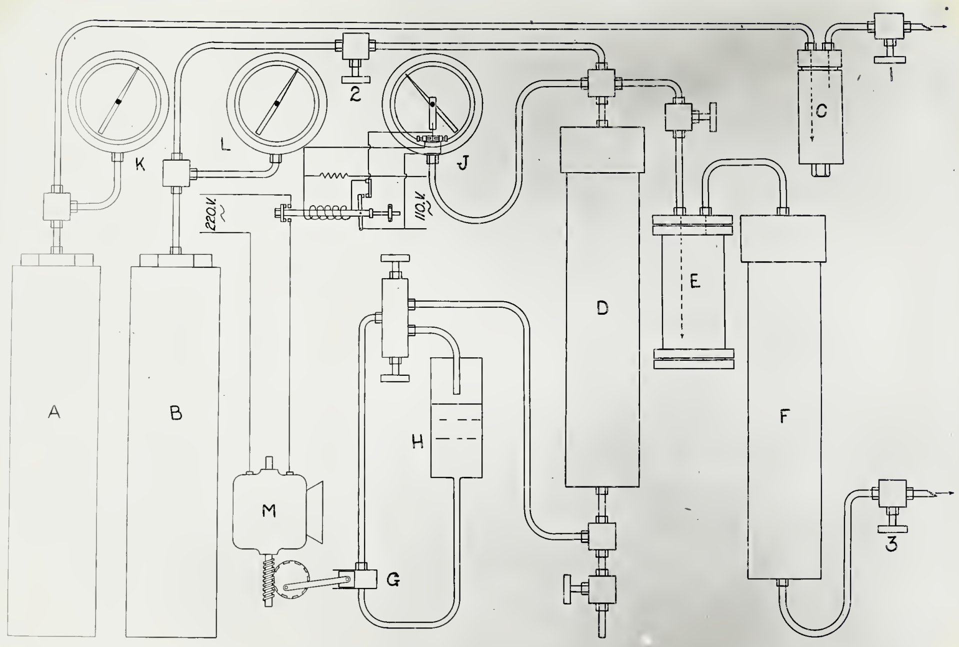
1
2
C
K
L
J
220.V ~
110.V ~
E
D
A
B
F
H
M
G
3

Figure 4.

High Pressure Storage and Control
System for Methane-Air Experiments.

The high pressure storage and control system for the methane-air experiments is shown diagrammatically in Figure 4. Gages ,K, and ,L, show the storage tank pressures. Both gases before compression into their storage tanks were passed over solid calcium chloride. The air storage ,A, was of such size that the pressure drop during a run was so small as to cause little difficulty in controlling the composition of the methane-air mixtures. Final purification of the air from carbon dioxide and water was obtained in the high pressure vessel ,C, containing flakes of sodium hydroxide. The air storage was connected by a valve 1 through a check valve to the control valve of the reacting system. The methane storage tank ,B, was connected through valve 2 to the pressure control tank ,D, scrubber ,E, and the subsidiary storage tank ,F,. The purifier ,E, contained, in order, calcium chloride and activated charcoal to remove traces of water and olefines in the gas.

Before making an experiment the air pressure was made at least 500 lbs. higher than the operating pressure to be used and only dropped slightly during the course of an experiment. However, the methane storage was of necessity small and means were devised to prevent any appreciable pressure drop during an

experiment. A hydraulic pump ,G, was used to introduce a 50% glycerine-water mixture from the reservoir ,H, into the pressure control tank ,D. The glycerine-water mixture did not dissolve excessive amounts of the gas and was without corrosive action on the metal parts. The operation of the pump was controlled as shown by the pressure in the tank ,D, through the high and low contacts on the gage ,J,. When the pressure dropped about 10 lbs. below the desired value the low contacts closed, energizing the relay shown which started the motor ,M. The consequent introduction of the liquid to the tank ,D, resulted in a pressure rise. When the pressure exceeded the desired operating pressure by about 10 lbs. the high contacts closed, the relay opened and pumping stopped. This method of pressure control was found highly satisfactory, total pressure variations being 20 lbs. or less which was without serious effect upon the control of the reaction mixture or the reaction temperature. The gas under constant pressure was connected by valve 3 through a check valve to the control valve of the reacting system.

The system used to control the oxidation reactions is shown diagrammatically in Figure 5. Photographs of the same apparatus are shown in Figures 6 and 7. The needle valves 1 and 2 used as control

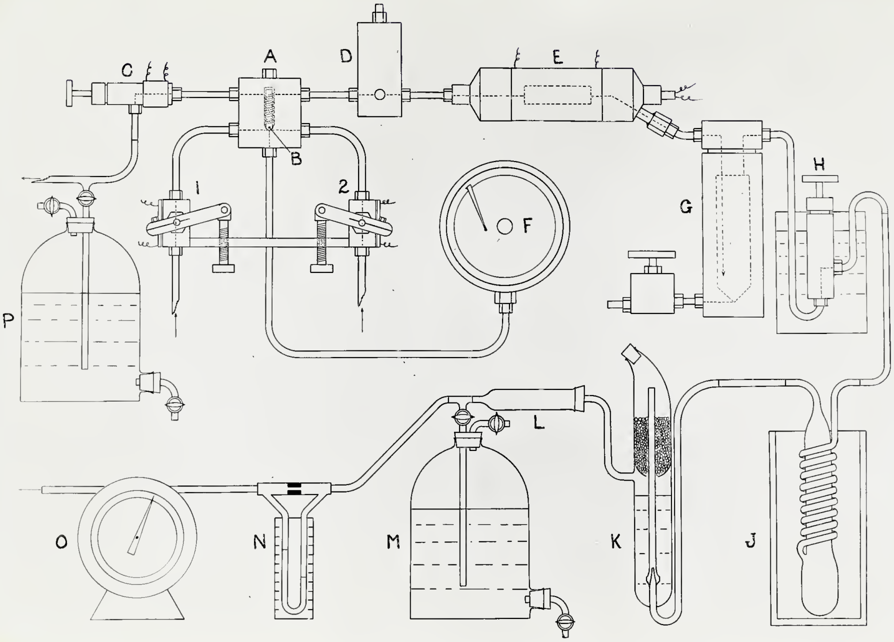
A
C
D
E
B
1
2
F
H
G
P
L
O
N
M
K
J

Figure 5.

Reaction, Condensing and
Collecting System.

valves admitted the gaseous hydrocarbon and air respectively to the apparatus. These control valves were electrically heated and maintained at a nearly constant temperature of about 90° C. An arrangement of adjusting screws was fitted to them in order that fine adjustment of the position of the valve stem was possible with consequent ease of control of gas flow. Heating these valves to a constant temperature was necessary to prevent freezing and to prevent changes in rate of flow due to temperature variations. The design was such that the valve stems did not rotate but moved only parallel to their axis. From the control valves the gases passed into the mixer ,A.

The mixer ,A, consisted essentially of two parts, a piston ,B, and the main body. The piston ,B, which had a spiral groove cut into it over its length, fitted snuggly into a hole drilled in the main body. The gases entered at the bottom of the piston ,B, and in travelling up the spiral groove were thoroughly mixed before entering the reactor ,E,. At the bottom of the piston was a seat which formed with the piston a check valve, in that, it prevented the mixed gases from entering either of the supply tanks should the operating pressure be suddenly raised by an explosion in the reactor. The check valves placed in each of the

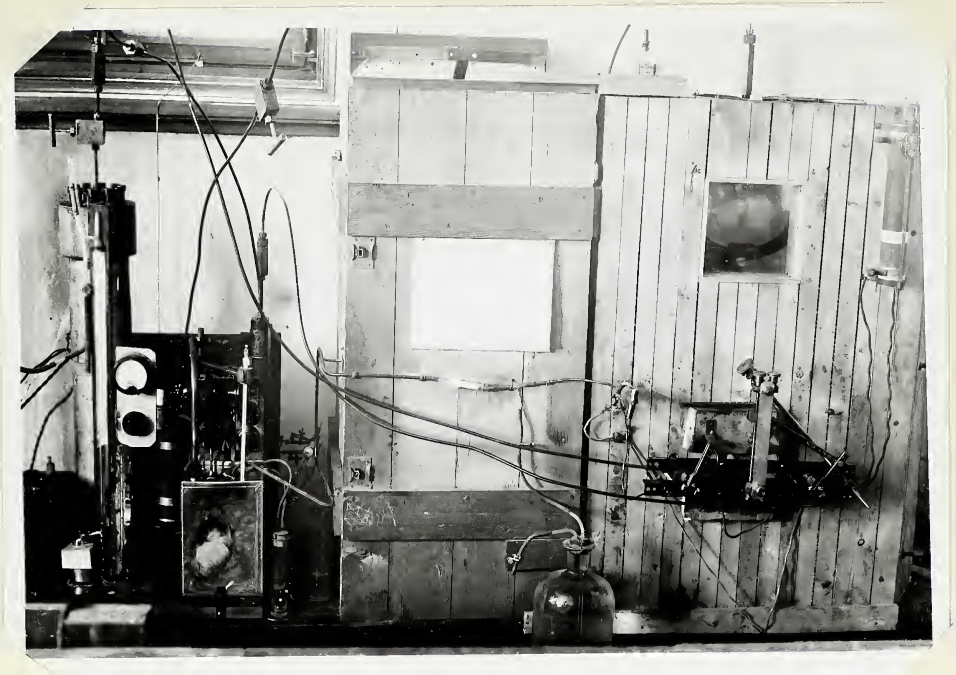

Figure 6.

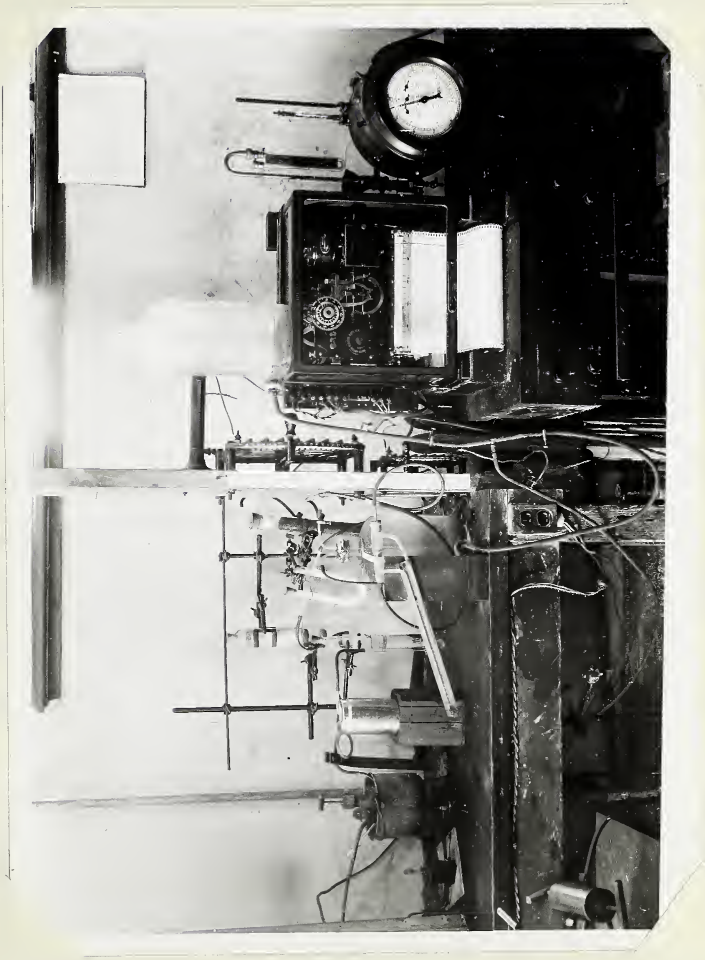

Figure 7.

high pressure supply lines acted as an additional precaution against mixed gases getting into the storage system. From the mixer ,A, a sample of the mixed gases was taken through the electrically heated expansion valve ,C, to the gas analyzer while the remainder was passed through the safety valve ,D, to the reactor ,E. A record of the pressure during a run was obtained by means of the recording pressure gage ,F. This gage was calibrated at intervals by comparison with a dead weight piston gage. The gas mixture after passing through the reactor ,E, was led directly to the bottom of the water-cooled high pressure bronze condenser ,G. This condenser was chromium-plated on the inside to prevent corrosion by the liquid products of the reaction. The gases leaving the high pressure condenser were expanded to atmospheric pressure through the heated expansion valve ,H. All tubing subsequent to the reactor and fittings were of copper or other non-ferrous metal to resist corrosion. The final removal of oxygenated compounds was affected by means of the ice condenser ,J, the water scrubber ,K, and the calcium chloride tube ,L. The flowmeter ,N, indicated the rate of off-gas flow and the total volume of gas passed was recorded by the calibrated wet test-meter ,O. A continuous sample of the inlet and off gases was obtained with the aid of the constant head sample bottles ,P, and ,M.

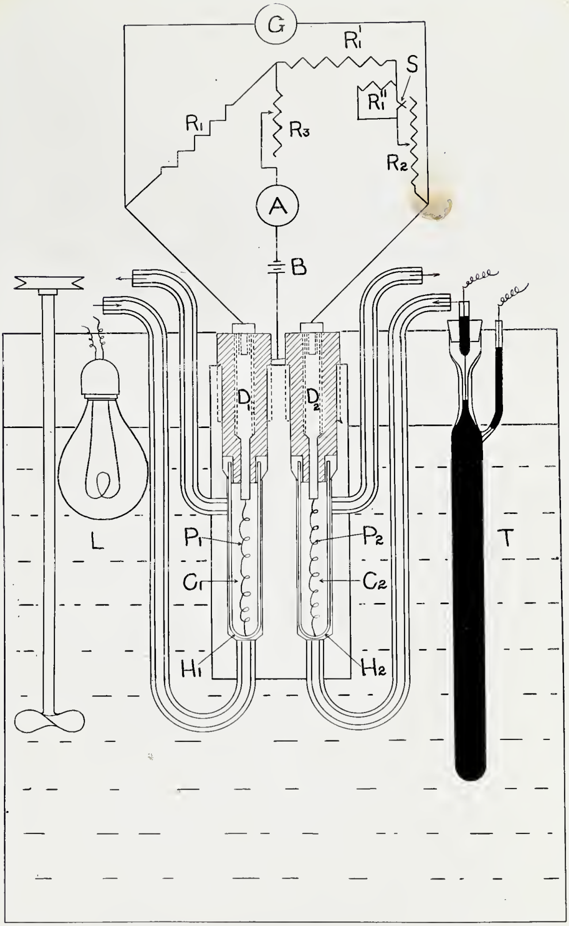
G
R1'
S
R1''
R1
R3
R2
A
B
D1
D2
L
P1
P2
C1
C2
T
H1
H2

Figure 8.

Continuous Gas Analyzer.

The composition of the inlet gas was obtained by means of a continuous gas analyzer shown in Figure 8. The gas analyzer was a combination of a thermal conductivity cell and a wheatstone bridge circuit. Its construction was a modification of the Shakespeare Katharometer. The two cells,C_1, and,C_2, of about 3.5 cc. volume were cut out of a single block of copper and contained the resistors ,P_1,and ,P_2, of 36 gauge platinum wire. Both platinum wires, coiled into a helix, were of identical resistance, about 1 ohm. The lower ends were connected to the brass hairpins ,H_1, and ,H_2, the other ends being connected to heavy brass rods ,D_1, and ,D_2, threaded through insulating bakelite plugs as shown. Copper tubes of 3/16'' outside diameter were soldered into both the cells ,C_1, and ,C_2, as shown to permit the passage of air and air mixtures into their respective cells. The gases were introduced through the bottom of the cells in order that they be given sufficient time to come to the bath temperature before coming into contact with the platinum wires. The rate of the gas flow in the two cells was not more than 10 cc./min, below which rate the readings were independent of the rate of gas flow. The bath temperature was kept constant by means of the thermostat ,T, which controlled a 40 watt lamp ,L, wired as heater. The bath contained mineral seal oil.

The electrical system was a wheatstone bridge, the platinum wires ,P_1, and ,P_2, forming two arms of the bridge. Resistances ,R_1, and ,R_1^1, were equal and about 45 ohms in magnitude. R_1^{11} and R_2 were 2.1 ohms and 4.0 ohms approximately. A galvanometer ,G, was placed across the arms and current was supplied by a battery ,B, connected in series with an ammeter ,A, and a rheostat ,R_3. The adjustable resistance ,R_2, was of the type of platinum wire in mercury (22). Resistance ,R_1^{11} , could be introduced into the circuit by means of switch ,S, and in this way altered the range of the instrument. In operating the gas analyzer a definite current was passed from the battery through the bridge with the result that the platinum wires were heated 100-200 °C. It was found by experience that the current must be kept below 0.58 amps, otherwise the air-hydrocarbon mixture ignited in the cell producing a marked discontinuity in the calibration curve. The bridge was balanced by the mercury slide-wire ,R_2, its setting depending upon the difference in resistance of the two platinum wires which,in turn, depended upon the thermal conductivity of the gas in the cells. The thermal conductivity of any gas mixture is a definite function of its composition and thus the composition could be determined. The instrument was calibrated on

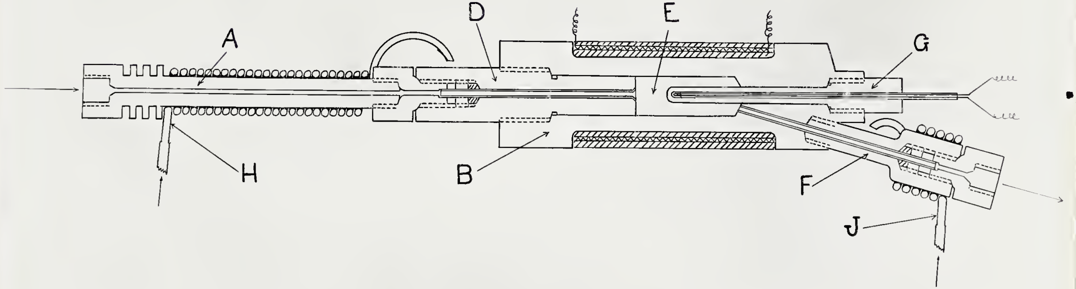

Figure 9.

Reactor.

several mixtures of two gases of known composition. For any particular current a graph could be plotted showing composition versus position of adjustable resistance ,R_2. One cell ,C_1, contained pure dry air as a reference gas,the unknown mixture of hydrocarbon and air being passed through cell ,C_2,. The instrument showed with ease a change in composition of 0.2% by volume of gas in air. During an experiment the resistance ,R_2, was set for the desired composition and the control valve 2 (Figure 5) adjusted in order to keep the galvanometer reading at zero indicating constant and desired composition.

The reactor ,E, is shown in detail in Figure 9. It consisted essentially of a main body ,B, which was constructed from high nickel-chromium-austenitic steel of such dimensions that the maximum safe working pressure was 4,000 lbs. at 500 °C: The mixture to be heated entered the reactor through the water-cooled extension ,A, by way of a glass tube in the plug ,D, to the catalyst chamber ,E. The products left by a glass tube through the outlet plug ,F, to the high pressure condenser. Cooling water passing through the copper coil ,H, kept the steel plug ,A, and the outlet end of the plug ,D, at a temperature below that necessary for reaction and similarly cooling water through the coil ,J, kept the

plug ,F, cooler than the reacting temperature. Consequently, the reacting gases were at reacting temperatures only in the catalyst chamber or when in contact with glass. This was found to be an essential procedure, otherwise reactions accurred in ,A, and in the outer end of ,F, resulting in carbon formation and uncertain results. The effective volume of the catalyst chamber was 12.7 cc. All interior surfaces were copper-plated to eliminate the possibility of ferrous surfaces contacting the reacting gases. It was found necessary to replate the interior of the reactor at frequent intervals because the copper plate scaled off on areas of the steel from time to time. The reactor was heated electrically by the winding shown and the temperature was measured by means of a calibrated Fe-Const. thermocouple placed in the thermocouple well ,G. Placing the thermocouple in an internal well permitted the temperature to be obtained at the centre of the catalyst chamber. The reaction temperature was maintained constant at any desired value, ± 2°C. by a potentiometric type of recording temperature controller.

The operating procedure in an experiment was developed and standardized with experience to give controlled operation and unambiguous results. The method of obtaining the desired mixture in the reactor consisted

essentially of connecting the gaseous hydrocarbon storage directly through one of the control valves, opening the expansion valve ,H, (Figure 5) to the approximate final desired position and adjusting the flow of air through the other control valve until the desired composition was obtained as shown by the composition of the gas bled to the analyzer through the valve ,C. A great deal of care was necessary in admitting the air since its pressure in the reactor must be kept below the operating pressure of the experiment, otherwise air would tend to pass into the hydrocarbon storage. The pressure in the reaction apparatus was always that of the gaseous hydrocarbon storage. Finally the expansion valve ,H, was set by reference to the off-gas flowmeter to give the desired rate of flow. The pressure during an experiment was maintained constant by operation of the hydraulic pump as described previously. A minimum excess pressure in the air storage of 500 lbs. was found to be necessary in order to provide satisfactory control on the inlet gas composition. When using natural gas its storage pressure was fixed initially at about 50 lbs. above the desired pressure. This procedure took care of the pressure drop during the preliminary process of adjusting the gas composition and gave an average pressure throughout the experiment of the desired value. The pressure drop

during an experiment was usually in the neighborhood of 75 lbs. During operations the expansion valve feeding the gas analyzer was so adjusted that the lag between a change in the gas composition in the mixer and its indication on the analyzer was about one minute. When flow rate, composition, pressure and temperature had all reached the desired steady states the high pressure condenser was blown out and the recovery system from the expansion valve ,H, (Figure 5) to the gas meter ,O, (Figure 5) connected. The inlet gas sample bottle and finally the off-gas sample bottle were connected. About fifteen minutes were allowed to elapse before connecting the off-gas sample bottle. The rate of flow of water from the sample bottles, and consequently the rate of sampling during an experiment was kept constant by use of a constant head aspirating device. In this manner a representative average sample of the off-gas was obtained. The volume of the off-gas sample was measured and added to the reading of the gas meter.

Analytical Methods.

At the conclusion of an experiment the liquid products were blown out of the high pressure condenser into the ice condenser. The gain in weight of each item in the recovery system and the total off-gas flow as

measured on the gas meter were recorded. In the majority of the experiments no liquid products were obtained in the ice condenser and it was very seldom that the water scrubber gained more than 0.04 gms. The efficiency of the water scrubber was tested by placing another scrubber after it in one of the runs and carrying out an analysis for the various oxidation products on its contents at the conclusion of the run. It was found that the amount of methyl alcohol, formaldehyde and formic acid recovered was less than 0.5 % of the amount obtained from the high pressure condenser and ice condenser. The contents of the calcium chloride tube were also examined. At the highest rate of flow used, the amount of oxidation products obtained was negligible. A faint odor of formaldehyde in the off-gas from the gas meter was shown to be of no consequence by measurements with a charcoal absorber in the line before the gas meter. These tests demonstrated conclusively the efficiency of the recovery system. The contents of the high pressure condenser, ice condenser and water scrubber were added to a 100 cc. volumetric flask and the whole made up to 100 cc. with distilled water. Aliquot portions were taken for the analysis of methyl alcohol, formaldehyde and formic acid.

The off-gas sample was collected over an

aqueous solution of 20 % sodium sulphate and 5% sulphuric acid. The inlet gas was collected over water. All analysis were carried out in duplicate in an improved Bureau of Mines type of apparatus. Carbon dioxide was determined in potassium hydroxide solution, olefines in fuming sulphuric acid and oxygen in alkaline pyrogallate solution. Carbon monoxide and hydrogen were determined by combustion over copper oxide at 300 °C, methane and ethane by slow burning with oxygen on a platinum filament. A Peterson compensating burette with mercury as confining liquid was used. Agreement between duplicate analysis was good. In connection with certain ambiguous experiments the off-gas was analyzed by another and more precise m method (19) similar in principle to the method of ultimate organic analysis with excellent agreement. Further, in order to remove any doubt as to the representative nature of the gas sample, analysis were occasionally carried out on instantaneous off-gas samples with satisfactory results showing that the off-gas did not change appreciably in composition during an experiment. Analysis of the gas samples after various intervals of storage over their respective confining liquids also showed no changes.

Methyl Alcohol Determination.

Only one method appears in the literature whereby methyl alcohol may be determined rapidly and

and quantititatively in a mixture of organic acids, aldehydes and esters. The method in question is that due to Fischer and Schmidt(16).

Essentially the procedure depends upon the formation of methyl nitrite which is not very soluble in acid and alkali and is consequently very easily volatilized. The liberated methyl nitrite is passed into an acidified solution of potassium iodide where it is saponified and the nitrous acid liberated reacts with the hydriodic acid forming free iodine. The iodine is then titrated with a standardized solution of sodium thiosulphate and subsequent calculations are based on the fact that one molecular weight of methyl alcohol is equal to one molecular weight of sodium thiosulphate as shown by the following reactions.

$$NaNO_2 + CH_3COOH \longrightarrow CH_3COO.Na + HNO_2$$

$$CH_3OH + HNO_2 \longrightarrow CH_3NO_2 + H_2O$$

$$2\ HNO_2 + 2\ HI \longrightarrow I_2 + 2\ NO + 2\ H_2O$$

$$I_2 + 2Na_2S_2O_3 \longrightarrow 2Na_2S_4O_6 + 2\ NaI$$

The method of Fischer and Schmidt as described by them did not give satisfactory results. Consequently, the author made investigations with the result that a slightly modified method was developed which will be shortly outlined. When strictly adhered to the results obtained were reliable and reproducible.

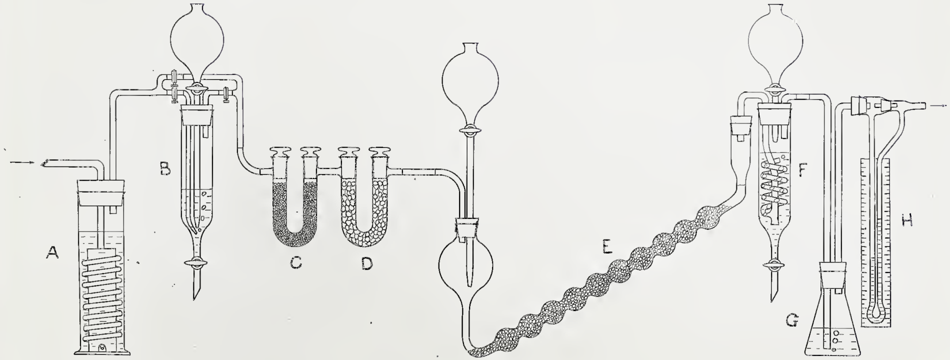

Figure 10.

Apparatus for Methyl
Alcohol Determinations.

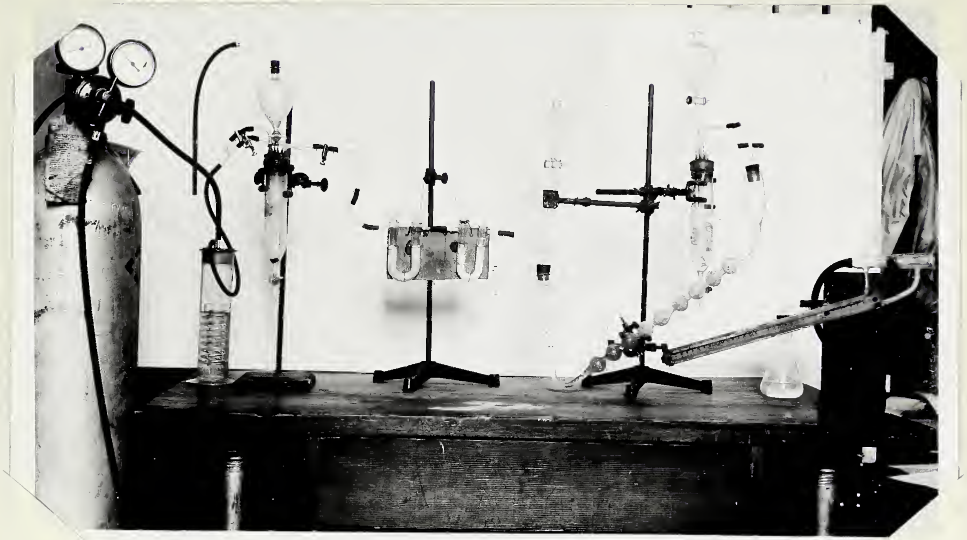

Figure 11.

Apparatus for Methyl
Alcohol Determinations.

The apparatus used in the determination of methyl alcohol is shown in Figure 10 and 11. It consisted essentially of a reaction flask ,B, a meyer tube ,E, and a guard flask ,F, The inert gas from the high pressure storage was passed through the scrubber ,A, containing water, before being introduced to the bottom of the reaction flask as shown. Carbon dioxide, nitrogen and methane were all found to be satisfactory for this purpose. Methane was used in most of the determinations since large quantities were available. A separatory funnel inserted on the top of the reaction flask permitted the introduction of the reactant while a drain cock at the bottom allowed the removal of the products. A by-pass permitted the reaction flask to be isolated at any time. The U-tubes ,C, and ,D, contained in order, solid sodium nitrite and sodium bicarbonate, their function being to convert any volatilized methyl alcohol to methyl nitrite and to remove oxides of nitrogen before the gases passed into the meyer tube containing an acidified solution of potassium iodide. It was found necessary to replace the sodium nitrite and sodium bicarbonate frequently and after doing so a blank determination was made. The guard flask ,F, contained an acidified solution of potassium iodide, its function being to saponify any methyl nitrite

which might escape through the meyer tube. A water trap ,G, prevented the accidental entrance of air into the apparatus since the success of this method depended upon the complete elimination of oxygen from the apparatus. The flowmeter ,H, measured the rate of gas flow.

In carrying out a determination the air is first displaced in the apparatus with the inert gas. To the guard flask and meyer tube are added 15 cc. of potassium iodide solution, containing 4 gms. of potassium iodide, 10 cc. of concentrated hydrochloric acid and finally distilled water to make the final volume in each case 30 cc. and 65 cc, respectively. The inert gas stream is then by-passed from the reaction flask into which is introduced a definite volume of the diluted condensate, 10 cc. of saturated sodium nitrite containing 4 gms. of urea and finally 20 cc. of 25% acetic acid. The reaction flask is then connected directly to the inert gas stream and the flow is adjusted to 150 cc. / min. The methyl nitrite formed is completely liberated in one hour but it is necessary at the end of that time to isolate the reaction flask from the system and continue passing the inert gas for 15 minutes to insure the complete removal of oxides of nitrogen. The contents of the iodine solutions are then combined and the liberated iodine is titrated with N/10 sodium thiosulphate. The value of the blank analysis is taken into consideration when

making a calculation.

Determinations made on known amounts of absolute methyl alcohol gave results showing better than 99% of the theoretical value. To obtain good results it was essential to keep the gas flow constant during an experiment, completely eliminate oxides of nitrogen and, finally, prevent any accidental access of air to the apparatus. All determinations were made in duplicate. The limit of error allowed between duplicate determinations was 0.5%.

Determination of Formaldehyde.

Formaldehyde was determined by Romijn's cyanide method (30) which is specific for this compound. The procedure for the determination of the excess potassium cyanide, outlined in Allen's organic analysis (1) was modified to permit a more rapid determination.

A 10 cc. portion of the diluted condensate is treated with excess potassium cyanide. For the quantities of aldehyde dealt with about 11 cc. of N/10 potassium cyanide are added. The potassium cyanide combines with the aldehyde forming a soluble addition compound, one molecule of aldehyde combining with one molecule of potassium cyanide. The whole is then added to 10 cc. of N/10 silver nitrate, acidified with concentrated nitric acid. The excess potassium cyanide combines with the

silver nitrate forming insoluble silver cyanide which is then filtered off. The filtrate is then made up to 100 cc. with distilled water and titrated with N/10 potassium thiocyanate using ferric alum as the indicator. A blank analysis is made and the difference between this blank result and that obtained by titrating the filtrate after the addition of the aldehyde solution gives the amount of N/10 sulphocyanate corresponding to the silver not precipitated by the excess cyanide. From this the amount of aldehyde can be calculated. This method is accurate in the presence of acetaldehyde providing the solution is titrated within a reasonable time after the addition of the potassium cyanide.

Determination of Formic Acid.

Formic acid was determined by titrating with standard alkali.

A 10 cc. portion of the diluted condensate is warmed to expel carbon dioxide and titrated with .05 N sodium hyroxide. In the majority of the samples copper formate is present. In these cases an excess of sodium hydroxide is added to 10 cc. of the diluted condensate, the whole heated to boiling, filtered to remove precipitated copper hydroxide and back titrated with .05 N sulphuric acid.

Combustion Analysis.

An ultimate organic analysis was made on some of the diluted condensates. This analysis was carried out to determine whether all the carbon was accounted for in the condensate by the chemical determinations. About a 5 cc. portion of the diluted condensate, whose density was previously determined was used as the sample. The method consisted of weighing a small glass bulb provided with a capillary, which after filling was sealed to prevent loss in weighing. The bulb was then placed in a boat, the tip of the capillary tube broken off and the whole placed into the combustion tube in the furnace. The remaining part of the analysis was identical with that used for solids as described by Fischer (15). All analyses showed conclusively that over 98% of the carbon in the condensates was present in the various oxidation products determined. This left no doubt as to the accuracy of the chemical analysis and further showed that the amount of other carbon compounds present was practically negligible.

EXPERIMENTAL RESULTS.

The results may be divided into two sections, namely, those dealing with natural gas-air mixtures on the one hand and methane-air mixtures on the other. The effect of temperature,rate of flow and inlet gas composition on the survival of the useful oxygenated compounds was determined for both mixtures while the effect of pressure was only determined for methane-air mixtures. The data obtained for the different variables is shown in the accompanying tables and no further explanation need be given here since, with the sample calculation given later, they are self explanatory. Unless otherwise stated, copper was used as the catalyst in all the experiments. Since the interior of the reactor was copper-plated the steel walls did not exert any catalytic influence. However, it must be born in mind that in using the other calalysts the copper lining of the catalyst chamber was always in contact with the reacting mixture. Many experiments are not tabled, several that were incomplete or subject to poisoning being left out together with many duplicate experiments.

All calculations were based on 100 litres of inlet gas at N.T.P. This was found necessary since in some experiments the volume of the off-gas differed a great deal from the volume of the inlet gas which made it impossible to draw comparisons as regards the total carbon

burned and the weight of the liquid products from the off-gas volumes. Since no means of direct determination of the in-gas volume were available, the volume conversion factor between the inlet gas and the off-gas was found by using a carbon balance. On the basis of many analytical tests of various kinds, it was concluded that carbon balances were reliable. Carbon balances were found to be more accurate than nitrogen balances since in most of the experiments the percentage of nitrogen in the off-gas was very small. A method of differences had to be used and small errors in nitrogen estimations would result in large errors in the balance calculated. The nitrogen balances agreed, however, within the limit of error. Oxygen balances, as will be pointed out later, were of no value, large surpluses and deficiencies occurring frequently. Traces of higher hydrocarbons were obtained in the off-gas for the majority of the methane-air experiments. However, since the percentage of the unknown hydrocarbons was very small all the carbon formed during the combustion analysis was attributed to methane.

The results of experiment 69 may be taken as typical and the necessary calculations are illustrated to show the method used. Calculations of the same type were made for all the experiments.

EXPERIMENT 69.

Data:-

In-Gas Analysis:-

O_2	10.33
CH_4	46.8
C_2H_6	1.21
N_2	41.66

Off-Gas Analysis:-

CO_2	2.15
O_2	0.68
H_2	1.16
CO	3.23
CH_4	45.1
N_2	47.56
C_2H_6	.12

Total Volume of off-gas at N.T.P. = 99.3 L.

Weight of products in condensate:-

CH_3OH	= 1.94 gms.
CH_2O	= .134
$HCOOH$	= .065
H_2O	= 9.52

Calculations:-

Grams of carbon in CH_3OH $= \frac{12}{32} \times 1.94 = .72$

Grams of carbon in CH_2O $= \frac{12}{30} \times .134 = .0537$

Grams of carbon in $HCOOH$ $= \frac{12}{46} \times .065 = .017$

Total = .798

Grams of carbon in off-gas $= \frac{50.72}{100} \times 12 \times \frac{99.3}{22.4} = 27.1$

Total weight of carbon in products = 27.9 gms.

Weight of carbon in 22.4 litres of in-gas

$= \frac{49.22 \times 12}{100} = 5.91$ gms.

$$\frac{\text{Volume in-gas}}{\text{Volume off-gas}} = \frac{27.90}{5.91} \times \frac{22.4}{99.3} = 1.068$$

Volume off-gas / 100 litres of in-gas at N.T.P.

$= \frac{100}{1.068} = 93.7$L.

Weight of products / 100 litres of in-gas at N.T.P.

CH_3OH $= \frac{93.7}{99.3} \times 1.94 = 1.84$ gms.

CH_2O $= \frac{93.7}{99.3} \times .134 = .126$

$$HCOOH = \frac{93.7}{99.3} \times .0650 = .0613$$

$$H_2O = \frac{93.7}{99.3} \times 9.52 = 8.98$$

Weight of condensate =11.01 gms.

Weight of carbon and Oxygen in liquid products:-

	Carbon	Oxygen
CH_3OH	.692	.92
CH_2O	.0504	.0672
$HCOOH$	.016	.0427
H_2O		8.00
Total	.758 gms.	9.03 gms.

Weight of carbon burned / 100 litres of in-gas at N.T.P.

$$\text{In Off-gas} = \frac{5.38}{100} \times 12 \times \frac{93.7}{22.4} = 2.70 \text{ gms.}$$

In condensate = .758

Total = 3.46 gms.

Yields as % of total carbon burned to:-

$$CH_3OH = \frac{.692 \times 100}{3.46} = 20.0$$

$$CH_2O = \frac{.0504}{3.46} \times 100 = 1.45$$

$$HCOOH = \frac{.016}{3.46} \times 100 = 0.46$$

Total 21.91

Total carbon in / 100 litres of in-gas

$$= \frac{49.22}{100} \times 12 \times \frac{100}{22.4} = 26.4 \text{ gms.}$$

% of total carbon in oxidized = $\frac{3.46}{26.4} \times 100 = 13.1$

Wt. of oxygen/100L.

$$\text{In-gas at N.T.P.} = \frac{10.33}{100} \times 32 \times \frac{100}{22.4} = 14.76 \text{ gms.}$$

Weight of oxygen in off-gas / 100 litres of in-gas:-

$$= \frac{4.44}{100} \times 32 \times \frac{93.7}{22.4} = 5.94 \text{ gms.}$$

	Table 1.						Table 1.A.		
Experiment No.	47	48	49	50	51	52	62	63	64
Temperature °C.	250	300	350	350	350	350	350	350	350
Pressure in atms.	142	137	147	150	150	199	185	185	185
Off Gas Flow L./Min.	0.96	0.97	0.80	0.51	0.84	0.84	0.76	0.77	0.98
In-Gas Analysis:									
O_2	15.0	14.8	14.9	14.9	15.0	14.8	6.81	8.62	3.53
CH_4	26.7	26.6	26.2	26.2	26.7	26.6	61.0	53.3	76.7
C_2H_6	0.85	0.88	0.87	0.87	0.85	0.88	2.02	1.76	1.93
N2	57.45	57.72	58.03	58.03	57.45	57.72	30.17	36.33	17.6
Off-Gas Analysis:									
CO_2	0.85	0.43	1.4	3.0	2.81	3.9	1.86	2.16	1.16
O_2	15.55	14.65	1.46	2.2	0.75	0.80	0.52	0.84	0.42
H_2			2.1	1.1	1.44	2.60	0.31	0.63	0.21
CO			3.0	3.8	4.02	4.40	1.67	2.27	0.79
CH_4			23.1	24.4	23.9	23.6	66.0	53.8	79.5
C_2H_6			2.2	0.4	0.49	0.80	0.80	0.70	0.54
N_2			66.8	65.1	66.6	63.9	28.8	39.6	18.2
$\frac{\text{Volume In-Gas}}{\text{Volume Off-Gas}}$:			1.22	1.15	1.13	1.19	1.11	1.07	1.03
Condensate, gms./100 L. in-gas at N.T.P.									
Total			9.07	9.34	9.43	11.76	8.17	9.29	4.08
CH_3OH			0.018	0.264	0.246	0.291	1.29	1.13	0.654
CH_2O			0.013	0.086	0.088	0.051	0.201	0.173	0.145
HCOOH							0.035	0.034	0.026
H_2O			9.04	8.99	9.10	11.42	6.64	7.95	3.25
% Alcohol in Condensate,			0.198	2.84	2.60	2.48	15.8	12.1	16.0
Carbon Oxidized, gms./100L,			1.94	3.30	3.36	3.87	2.27	2.73	1.33
Carbon to Compounds, gms,/ 100 L,			0.012	0.134	0.128	0.131	0.503	0.575	0.312
% of Total Carbon In Oxidized,			13.0	22.1	22.1	25.6	6.52	8.96	3.07
Yields as % of Total Carbon Burned to:									
CH_3OH			0.348	3.01	2.76	2.84	21.4	15.5	18.6
CH_2O			0.275	1.04	1.05	0.53	3.55	2.55	4.4
HCOOH							0.32	0.40	0.51
Total			0.623	4.05	3.81	3.35	25.35	18.37	23.54
Yields as % of Total Inlet Oxygen to:									
CH_3OH			0.042	0.621	0.577	0.692	6.69	4.57	6.21
CH_2O			0.034	0.215	0.22	0.13	1.11	0.75	1.54
HCOOH							0.191	0.251	0.36
H_2O			38.1	37.6	38.0	48.4	61.0	57.6	57.5
Total			38.18	38.44	38.8	49.22	69.05	63.11	65.61
% of Total Inlet Oxygen Accounted for:			62.3	79.8	71.6	88.4	98.2	108	120

Oxygen in condensate = 9.03

Total = 14.97 gms.

% of oxygen accounted for $= \frac{14.97}{14.76} \times 100$

$= 101.2$

Yields as % of total inlet oxygen to:-

$CH_3OH = \frac{.92}{14.76} \times 100 = 6.23$

$CH_2O = \frac{.0672}{14.76} \times 100 = .455$

$HCOOH = \frac{.0427}{14.76} \times 100 = .288$

$H_2O = \frac{8.00}{14.76} \times 100 = 54.2$

Total 61.17

Natural Gas.

Preliminary experiments made on natural gas-air mixtures are shown on Table 1. These experiments were made with oxygen and the gaseous paraffins present in the natural gas in the approximate stoichiometrical proportions for the formation of methyl alcohol. Experiments 47, 48, and 49 were made to determine the initial ignition temperature of the natural gas. At temperatures of 250 °C. and 300 °C. shown in experiments 47 and 48, the operating temperature was too low to produce any appreciable oxidation of the natural gas. The large survival of oxygen and the small percentage of carbon dioxide in the off-gas with the non-appearance of any liquid products illustrates this very well.

However, on raising the temperature to 350 °C. a vigorous reaction took place accompanied by explosions. These could be detected easily by the releasing of the safety valve and were distinctly audible being accompanied by a sharp metallic click in the reactor. During the explosions a copious layer of carbon was deposited on the catalyst. This deposit of carbon was probably formed in part by pyrolysis of methane in contact with hot metal and by the reactions postulated by Bone (7) to explain the results of explosions of methane under pressure. The amount of heat liberated during these explosions was enormous, bearing in mind the large mass of the reactor and the small amount of oxygen involved, since the recorder temperature rose as high as 20 degrees above the operating temperature. The explosive reaction was apparently stimulated by steel surfaces and in future experiments the inlet and outlet plugs of the reactor were cooled with water. By this procedure the explosions of the mixture were prevented except over copper in the reactor and the survival of the useful oxygenated products was increased. In all the reactions where explosions did not occur, no trace of carbon was found in the reactor, its fittings or on the catalyst. This is very well shown in Table 1 by comparing experiments 50-52 inclusive with experiment 49 in which the cooling coils were not attached. The condensate in all the

Table 11.

Experiment No,	76	77	66	67	60	69	58	59
Temperature °C.	350	--	--	--	--	--	--	--
Pressure in Atms.	185	--	--	--	--	--	--	182
Off-Gas Flow L./min.	0.85	0.78	0.84	0.86	0.83	0.83	0.80	0.82
In-Gas Analysis:								
O_2	3.47	3.76	6.15	8.45	10.8	10.33	12.0	13.2
CH_4	78.0	76.4	63.8	54.0	43.8	46.8	38.8	33.4
C_2H_6	1.02	1.88	2.11	1.79	1.45	1.21	1.21	1.1
N_2	17.51	17.96	27.94	35.76	43.95	41.66	47.99	52.3
Off-Gas Analysis:								
CO_2	0.53	0.61	1.26	1.76	3.29	2.15	3.31	3.52
O_2	0.21	0.32	0.21	0.74	0.55	0.68	0.65	0.52
H_2	0.53	0.47	0.56	0.82	0.53	1.16	1.17	1.03
CO	1.36	1.21	1.98	2.57	1.22	3.23	2.11	1.97
CH_4	78.7	77.8	68.1	55.8	47.1	45.1	40.1	34.2
C_2H_6	0.65	1.1	0.38	0.31	0.51	0.12	0.1	0.63
N_2	18.08	18.49	27.5	38.0	46.8	47.56	52.6	58.13
Volume In-Gas / Volume Off-Gas:	1.04	1.04	1.1	1.08	1.15	1.07	1.14	1.17
Condensate, gms./100 L In-gas at N.T.P.								
Total	4.73	4.42	7.48	8.60	9.28	11.01	10.14	9.80
CH_3OH	1.74	1.73	2.16	2.06	1.46	1.84	1.37	0.96
CH_2O	0.195	0.198	0.202	0.159	0.137	0.126	0.114	0.101
HCOOH	0.034	0.031	0.049	0.063	0.015	0.061	0.016	0.011
H_2O	2.76	2.46	5.07	6.32	7.67	8.98	8.64	8.73
% Alcohol in Condensate,	36.9	39.0	28.8	23.9	15.7	16.7	13.5	9.82
Carbon Oxidized, gms. / 100 L.	1.68	1.68	2.45	3.0	2.7	3.46	3.12	2.93
Carbon to Compounds, gms,/ 100 L,	0.742	0.739	0.904	0.856	0.608	0.758	0.565	0.402
% of Total Carbon In Oxidized,	3.94	3.92	6.73	9.73	10.8	13.1	14.2	15.3
Yields as % of Total Carbon burned to:								
CH_3OH	38.7	38.8	33.2	25.9	20.3	20.0	16.5	12.34
CH_2O	4.64	4.75	3.32	2.12	2.02	1.45	1.46	1.39
HCOOH	0.52	0.48	0.52	0.51	0.14	0.46	0.14	0.10
Total	43.86	44.03	37.04	28.54	22.46	21.91	18.1	13.73
Yields as % of Total Inlet Oxygen to:								
CH_3OH	17.5	16.1	12.26	8.54	4.75	6.23	4.02	2.55
CH_2O	2.1	1.97	1.23	0.70	0.473	0.455	0.356	0.288
HCOOH	0.473	0.401	0.385	0.365	0.068	0.288	0.066	0.059
H_2O	49.4	40.8	51.5	46.8	44.1	54.2	45.1	41.2
Total	69.47	59.27	65.38	56.41	49.39	61.17	49.54	44.08
% of Total Inlet O_2 Accounted for:	107.0	99.0	101.4	95.0	85.0	101.2	86.3	81.5

experiments consisted mainly of water with only small quantities of the useful oxygenated compounds. The weight of the condensate in experiments 51 and 52 was about the same, namely, 9.4 gms. The two experiments were made with different rates of off-gas flow and yet the yields of the useful products obtained did not differ appreciably. The percentage of inlet carbon burned was 22.1. An increase in pressure from 150-199 atmospheres shown by experiment 52 did not change the yield of useful products or the weight of the condensate to any great extent. However, the percentage of the total inlet carbon burned was increased from 22.1-25.6. The experiments at this high oxygen concentration were not very promising but they showed that a low concentration of the natural gas or a high concentration of oxygen was detrimental to the survival of the useful oxygenated products.

Effect of Inlet Oxygen Concentration.

The effect of inlet oxygen concentration on the survival of the useful oxygenated compounds is shown in Table 2. The percentage of the total carbon burned surviving in the total oxygenated compounds and alcohol with respect to the inlet oxygen concentration is shown by Graphs 1 and 2 on Figure 12. The yields fall off linearly with an increase in oxygen concentration in

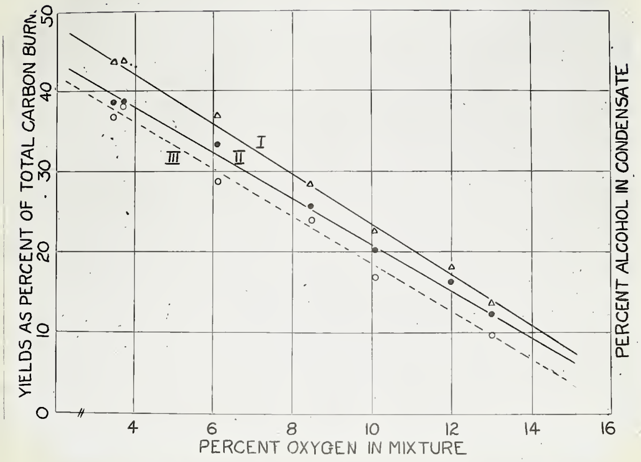
YIELDS AS PERCENT OF TOTAL CARBON BURN.
0
10
20
30
40
50
PERCENT ALCOHOL IN CONDENSATE
4
6
8
10
12
14
16
PERCENT OXYGEN IN MIXTURE
I
II
III

Figure 12.

the mixture. The conversion of the total carbon burned to the total oxygenated compounds and methyl alcohol was 44.03% and 38.8% at 3.76% oxygen concentration while at 13.2% oxygen concentration 13.73% and 12.34%, respectively. An increase in the oxygen concentration in the mixture decreased the amount of carbon going to formaldehyde and formic acid to a lesser extent than the amount going to methyl alcohol. This is shown very well in Figure 12, in that, the Graphs 1 and 2 tend to converge at higher oxygen concentrations.

The percentage of alcohol in the condensate in relation to the inlet oxygen concentration is shown by Graph 3 in Figure 12. The percentage of alcohol in the condensate drops off linearly with an increase in the oxygen, the straight line paralleling the yield almost exactly. A low oxygen concentration in the mixture was essential in obtaining a high percentage of alcohol in the liquid products as well as a high yield.

Graphs 1 and 2 shown in Figure 13 show the relationship existing between the grams of carbon oxidized per 100 liters of inlet gas and the percent of total in-carbon oxidized plotted against the inlet oxygen concentration. They measure, of course, the same thing and show increased methane consumption with increased oxygen concentration as might be expected.

They are of interest when considered in conjunction with the graphs of Figure 12, showing decreased yields of useful products with increasing oxygen concentration. As the percent of carbon burned increases from 4 to 8, the yield drops from 45% to 30% approximately, the oxygen going from 3 to 8%.

The oxygen survival was small and varied, relatively, greatly showing no relationship with the yields or in-gas oxygen content. The same result was obtained with the carbon monoxide and dioxide as individuals in the off-gas analysis. However, the combined oxides of carbon increased with an increase in the inlet oxygen concentration. The percentage conversion of oxygen to useful products was always smaller than the conversion of methane but followed in general the same course, the conversion decreasing with increasing oxygen concentration. The erratic variation in oxygen recovery, varying widely from less than to more than 100% was inexplicable. The phenomena will be discussed more fully later.

During the experiments shown in Table 2 the catalyst was poisoned frequently and this necessitated its removal from the reactor to be cleaned. A low conversion of carbon to useful compounds was a good indication in showing that the catalyst was working inefficiently. Some results obtained by using a

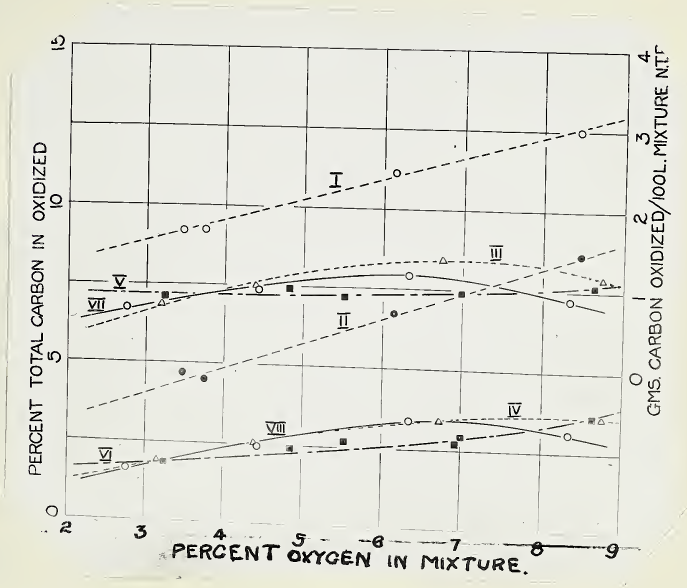
15
10
5
0
PERCENT TOTAL CARBON IN OXIDIZED
4
3
2
1
0
GMS. CARBON OXIDIZED/100L. MIXTURE N.T.P.
I
II
III
IV
V
VI
VII
VIII
2
3
4
5
6
7
8
9
PERCENT OXYGEN IN MIXTURE.

Figure 13.

	Table 3.			Table 3A.			
Experiment No.	55	59	53	77	80	81	79
Temperature ° C.	350	350	350	350	350	350	350
Pressure in atms.	188	182	168	185	188	185	188
Off-Gas Flow L. /Min.	0.62	0.82	0.93	0.78	1.0	1.04	1.30
In-Gas Analysis:							
O_2	12.68	13.2	12.9	3.76	3.68	3.66	3.73
CH_4	35.56	33.4	34.9	76.4	75.3	75.4	75.3
C_2H_6	1.19	1.1	1.15	1.88	2.42	2.63	2.66
N_2	50.57	52.3	51.05	17.96	18.6	18.31	18.31
Off-Gas Analysis:							
CO_2	3.6	3.52	3.0	0.61	1.07	0.95	2.45
O_2	0.7	0.52	0.3	0.32	0.21	0.21	0.5
H_2	0.8	1.03	2.7	0.47	0.42	0.53	0.5
CO	2.9	1.97	4.3	1.21	1.08	1.24	1.21
CH_4	36.4	34.2	33.8	77.8	78.5	77.6	75.0
C_2H_6	0.2	0.63	0.2	1.1	0.81	1.5	1.48
N_2	55.4	58.13	55.7	18.49	17.9	17.97	18.86
Volume In-Gas / Volume Off-Gas:	1.17	1.17	1.14	1.04	1.04	1;04	1.03
Condensate, gms./ 100L. In-gas at N.T.P.							
Total.	11.23	9.80	11.04	4.42	4.56	4.26	4.17
CH_3OH	1.30	0.96	1.06	L.73	1.60	1.72	1.83
CH_2O	0.127	0.101	0.103	0.198	0.166	0.151	0.185
HCOOH	0.014	0.011	0.016	0.031	0.037	0.040	0.033
H_2O	9.79	8.73	9.88	2.46	2.76	2.35	2.11
% Alcohol in Condensate,	11.6	9.82	9.58	39.0	35.1	40.3	44.0
Carbon Oxidized, gms/ 100 L.	3.52	2.92	3.87	1.68	1.78	1.86	2.67
Carbon to compounds, gms,/ L,	0.544	0.402	0.446	0.739	0.68	0.716	0.771
% of Total Carbon IN Oxidized,	17.3	15.3	19.5	3.92	4.16	4.31	6.17
Yields as % of Total Carbon Burned to:							
CH_3OH	13.9	12.34	10.3	38.8	33.8	34.6	25.8
CH_2O	1.44	1.39	1.06	4.75	3.72	3.25	2.77
HCOOH	0.11	0.1	0.1	0.48	0.54	0.57	0.32
Total	15.45	13.73	11.46	44.03	38;06	38.32	28;9
Yields as % of Total Inlet Oxygen to:							
CH_3OH	3.60	2.55	2.89	16.1	15.3	16.5	17.3
CH_2O	0.375	0.288	0.277	1.97	1.68	1.55	1.86
HCOOH	0.055	0.04	0.054	0.401	0.49	0.536	0.425
H_2O	48.3	41.2	44.2	40.8	46;9	40.2	35.3
Total	52.33	44.08	47:42	59.27	64.4	58.79	54.89
% of Total Inlet Oxygen Accounted for:	92.2	81.5	88.4	99.0	111.0	Lo5.0	L46;0

poisoned catalyst are shown on Table 1A. Three experiments were made at different oxygen concentrations and by comparing them with identical experiments in Table 2 the lower efficiency of the carbon conversion is at once obvious. For example, at 3.47% inlet oxygen, Experiment 76, the total yield to the useful oxygenated compounds based on carbon was 43.86% when the catalyst was working efficiently but when poisoned, as in Experiment 64 with 3.53% oxygen, the yield dropped to 23.53%. In these experiments with natural gas the catalyst was poisoned frequently and great care was necessary to keep the purification system working efficiently. It appeared to be essential that undesirable products from the sulphuric acid scrubber be eliminated. It was also found necessary to keep the reacting system free from oil and other higher gaseous hydrocarbons. There exists a possibility that the catalyst was mildly poisoned or somewhat inactive in all these experiments. Its effectiveness was however reproducible.

Effect of Rate of Flow.

The effect of rate of flow on the survival of the useful oxygenated compounds is shown in Figure 14 and the results are shown in Tables 3 and 3A. Graphs 1 and 2 in Figure 14 show the yields of the total oxygenated compounds and methyl alcohol at 3.7% inlet oxygen while

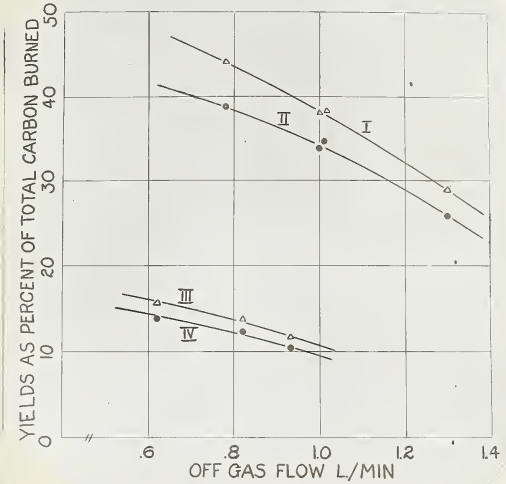
YIELDS AS PERCENT OF TOTAL CARBON BURNED
0
10
20
30
40
50
.6
.8
1.0
1.2
1.4
OFF GAS FLOW L./MIN
I
II
III
IV

Figure 14.

Graphs 3 and 4 show the effect at 13.0% inlet oxygen. = The flow rates are those of the off-gas at N.T.P. and cannot be used to calculate space velocities in the reactor. They are of comparative value however and are certainly known. All the experiments were made at 350 °C. and at a pressure of approximately 185 atmospheres. Within the range investigated the yield decreases with an increase in off-gas flow, an effect more noticeable at the lower oxygen concentration. Graphs 3 and 4 are not particularly reliable because of pressure changes in successive experiments.

The percantage of alcohol in the condensate did not change appreciably with an increase in off-gas flow rate. In experiments 77-79 inclusive,shown on Table 3A the percent of alcohol in the condensate increased from 39.0 to 44.0 with an increase in the rate of off-gas flow from 0.78 to 1.30 litres per minute. These experiments were made at a low inlet oxygen concentration. However, at high inlet oxygen concentrations the percent of alcohol in the condensate decreased from 11.6 to 9.58 with a change in the rate of off-gas flow from 0.62 to 0.93 litres per minute. The results of these experiments are shown in Table 3. The changes in alcohol concentrations are relatively small.

The total weight of the liquid products

Table IV.

Experiment No.	72	73	74	75
Temperature°C.	350	350	350	350
Pressure In Atms.	185	185	185	185
Off-Gas Flow L./min.	0.87	0.68	0.79	0.71
In-Gas Analysis:				
O_2	3.95	3.82	3.80	3.69
CH_4	74.8	74.7	75.5	75.7
C_2H_6	2.05	2.24	2.0	1.93
N_2	19.2	19.24	18.62	18.68
Off-Gas Analysis:				
CO_2	1.92	1.40	0.84	0.74
O_2	0.34	0.32	0.38	0.53
H_2	0.42	0.35	0.42	0.37
CO	0.85	0.84	1.35	1.27
CH_4	76.7	77.6	77.7	76.7
C_2H_6	1.40	1.39	0.97	1.1
N_2	18.37	18.10	18.34	19.29
$\frac{\text{Volume In-Gas}}{\text{Volume Off-Gas}}$:	1.06	1.06	1.05	1.03
Condensate, gms./100 L. In-gas at N.T.P.				
Total	3.83	3.88	4.20	4.06
CH_3OH	1.09	1.30	1.68	1.64
CH_2O	0.144	0.156	0.18	0.175
HCOOH	0.019	0.023	0.032	0.033
H_2O	2.58	2.40	2.31	2.21
% Alcohol in Condensate,	28.6	33.5	40.0	40.3
Carbon Oxidized, gms,/100 L.	1.88	1.69	1.83	1.73
Carbon to compounds, gms,/100 L.	0.477	0.56	0.714	0.696
% of Total Carbon In Oxidized,	4.45	4.0	4.3	4.07
Yields as % of Total Carbon Burned to:				
CH_3OH	22.0	29.0	34.5	35.6
CH_2O	3.06	3.7	3.94	4.03
HCOOH	0.26	0.35	0.45	0.5
Total	25.32	33.05	39.0	40.13
Yields as % of Total Inlet Oxygen to:				
CH_3OH	9.77	11.96	15.4	15.6
CH_2O	1.36	1.53	1.76	1.78
HCOOH	0.232	0.288	0.403	0.44
H_2O	40.7	39.4	37.8	37.4
Total	52.06	53.18	55.36	55.22
% of Total Inlet O_2 Accounted for:	116.0	106.0	102.7	105.0

changed very slightly with a change in the off-gas flow. At low inlet oxygen concentrations the condensate decreased from 4.42 to 4.17 gms. This is shown in Table 3A. On the other hand at a high inlet oxygen concentration a minimum weight of condensate was obtained in the range of flow investigated as shown by Experiment 59 in Table 3. An unexpected result was in the negligible relative variation in formaldehyde and formic acid production. One might expect these higher oxidized products to decrease, relatively, with increasing rate of flow.

Table 4 shows a series of experiments made with a poisoned catalyst while investigating the effect of rate of flow on the yields of the useful products. The catalyst was poisoned in Experiment 72 and it is interesting to note that in the following experiments the yields based on the total carbon burned increased with the use of the catalyst. This effect suggested that the impurity causing the poisoning of the catalyst was gradually removed. However,the normal yield (Experiment 77, Table 2) was not obtained until the reacting system was taken apart, cleaned with ether and the catalyst purified before making any further experiments.

Effect of Temperature.

The effect of temperature at 12.7% inlet oxygen

Table V. Table VA.

Experiment No.	57	53	56	92	86	87	93	88	85	31
Temperature °C	325	350	375	325	325	325	350	350	400	425
Pressure in Atms.	180	168	178	185	185	185	185	186	185	185
Off-Gas Flow L./Min.	0.8	0.93	0.86	0.9	0.95	1.0	0.94	1.08	0.94	1.00
In-Gas Analysis:										
O_2	12.7	12.9	12.5	3.98	4.1	3.89	4.22	3.63	3.71	3.68
CH_4	35.7	34.9	36.4	73.65	72.2	74.7	72.35	77.1	73.8	77.1
C_2H_6	1.2	1.15	1.2	2.73	2.76	2.14	3.20	2.61	2.03	2.0
N_2	50.4	51.05	49.9	19.64	20.94	19.27	20.23	17.24	19.88	17.2
Off-Gas Analysis										
CO_2	3.0	3.0	2.6	0.63	0.58,	0.58	0.74	0.47	0.53	.42
O_2	2.6	0. 3	0.6	0,39		0.19	0.21	0.19		0.0
H_2	1.3	2.7	2.4	0.47	0.63	0.50	0.37	0.56	0.53	
CO	2.5	4.3	5.5	0.14	0.63	0.73	0.21	0.63	0.53	C.797
CH_4	37.7	33.8	34.3	74.6	74.9	75.8	73.1	78.75	75.1	
C_2H_6		0.2	0.3	2.53	1.81	2.01	3.45	1.79,	2.68	
N_2	52.9	55.7	54.3	21.24	21.45	20.2	21.92	17.61	20.63	
Volume In-Gas / Volume Off-Gas:	1.16	1.14	1.09	1.03	1.03	1.02	1.05	1.05	1.05	1.00
Condensate, gms/100L. In-gas at N.T.P.										
Total	9.89	11.04	13.47	4.40	5.36	5.06	4.65	4.20	4.85	5.31
CH_3OH	0.953	1.06	0.695	1.70	2.20	2.12	1.80	1.83	1.97	2.06
CH_2O	0.153	0.103	0.093	0.147	0.194	0.187	0.153	0.224	0.198	.094
HCOOH	0.008	0.016	0.024	0.026	0.063	0.057		0.028	0.02	.01
H_2O	8.78	9.88	12.66	2.53	2.90	2.70	2.70	2.12	2.66	3.15
% Alcohol in condensate,	9.62	9.58	5.16	38.6	41.0	41.9	38.7	43.4	40.6	38.8
Carbon Oxidized, gms/100 L.	2.99	3.87	4.29	1.10	1.55	1.57	1.22	1.35	1.37	—
Carbon to compounds Gms./100 L,	0.437	0.446	0.306	0.703	0.922	0.89	0.738	0.785	0.826	—
% of Total Carbon In Oxidized,	14.7	19.5	20.6	2.6	3.73	3.72	2.90	3.10	3.24	—
Yields as % of Total Carbon Burned to:										
CH_3OH	12.0	10.3	6.1	58.0	53.3	51.0	55.5	51.0	54.3	—
CH_2O	2.04	1.06	0.86	5.53	5.02	4.77	5.0	6.65	5.75	—
HCOOH	0.143	0.1	0.14	0.62	1.06	0.95		0.54	0.37	—
Total	14.2	11.46	7.10	64.15	59.38	56.72	60.5	58.19	60.42	
Yields as % of Total Inlet Oxygen to:										—
CH_3OH	2.62	2.89	1.95	15.0	18.83	19.14	15.12	17.8	18.72	—
CH_2O	0.448	0.277	0.278	1.38	1.78,	1.82	1.36	2.31	2.0	
HCOOH	0.029	0.054	0.092	0.322	0.755	0.715		0.372	0.257	
H_2O	42.8	44.2	63.3	35.2	44.2	43.3	40.2	36.8	45.0	—
Total	45.9	47.42	65.62	51.9	65.56	65.0	56.7	57.28	66.0	—
% of Total Inlet O_2 Accounted for:	93.0	88.4	107.0	78.5	87.0	88.6	81.0	83.0	87.0	

, Experiments 53, 56, and 57, is shown in Table 5. A considerable drop in yield accurred with an increase in temperature . The yield of useful compounds based on the total carbon burned fell from 14.2 to 7.1% for a 50° rise from 325 to 375°C., while the oxygen conversion to the liquid products increased from 45.9 to 65.62%. The increase was mostly as water. The percentage of alcohol in the condensate decreased and the percentage of the inlet carbon burned increased with a rise in temperature. More ethane survived at the higher temperatures as shown by the off-gas analysis. Higher temperatures should favour the complete oxidation of the ethane with respect to the methane, since of the two gaseous paraffins ethane has the lower ignition temperature. The results suggest the formation of higher hydrocarbons in the reactions rather than survival of ethane. The percentage of carbon monoxide in the off-gas increased with a rise in temperature while the percentage of carbon dioxide remained practically constant. This series of experiments showed that at high inlet oxygen concentrations a low operating temperature was necessary to obtain higher yields of the useful oxygenated compounds.

Table 5A shows a series of experiments made to determine the effect of temperature on the yields of the oxygenated products at a lower inlet oxygen concentration'

namely, about 3.9%. Higher yields were obtained than in previous experiments shown in Table 2, using similar operating conditions suggesting an improvement in the catalyst with age. Experiments 77 and 93 shown in Tables 2 and 5 A show the increased yield very well. This series of experiments presented other peculiar results for which no explanation could be obtained. They were the last experiments made with natural gas. Practically all the ethane survived in these experiments. This was very unexpected since in most of the previous experiments only a small percentage of the original ethane survived. The procedure used in making these experiments was exactly the same as in previous experiments and no explanation is forthcoming to explain this peculiar behaviour. One may look to the catalyst surface as the source of this peculiarity and assign to it the power of preferentially oxidizing the methane. Duplicate experiments made at the same temperature did not check satisfactorily which was expected since different amounts of ethane were burned each time. No definite relation between temperature and yield was obtained. The amount of the total inlet carbon burned was about 3% while the amount of alcohol in the liquid products remained in the neighborhood of 40% by weight. At 425°C. unknown compounds in the off-gas, probably higher hydrocarbons, interferred with the carbon monoxide and hydrogen determinations with the result that

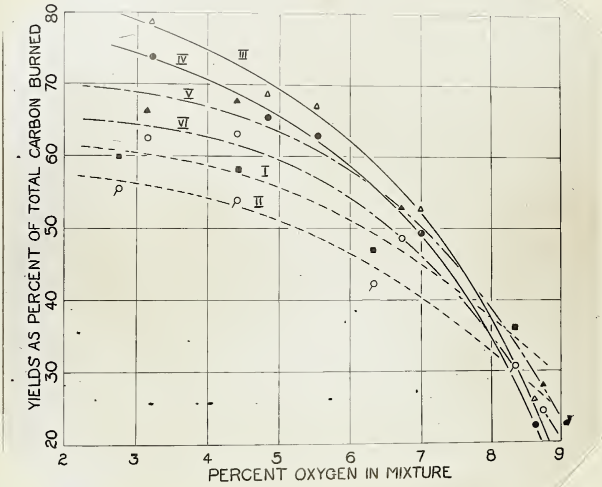
YIELDS AS PERCENT OF TOTAL CARBON BURNED
20
30
40
50
60
70
80
PERCENT OXYGEN IN MIXTURE
2
3
4
5
6
7
8
9
I
II
III
IV
V
VI

Figure 15.

Table VI.

Experiment No.	115	99	116	117	118	119	137
Temperature °C	475	475	475	475	475	475	475
Pressure in Atms.	184	184	184	184	184	184	184
Off-Gas Flow L./min.	0.84	0.80	0.81	0.77	0.83	0.79	0.78
In-Gas Analysis:							
O_2	3.22	4.86	5.53	6.93	7.6	7.9	8.63
CH_4	80.0	72.5	69.1	63.0	62.7	56.9	55.4
N_2	16.78	22.65	25.37	30.07	30.3	35.2	35.97
Off-Gas Analysis:							
CO_2	0.34	0.58	0.63	0.87	0.95	0.97	1.37
O_2	0.16	0.47	0.32	0.32	0.13	0.24	0.13
H_2	0.26	0.26	0.37	0.45	0.05	0.58	1.84
CO						0.11	0.21
CH_4	81.4	74.9	72.9	66.4	66.6	61.5	58.6
N_2	17.84	23.79	25.78	31.96	32.27	36.6	37.85
$\frac{\text{Volume In-Gas}}{\text{Volume Off-Gas}}$:	1.04	1.04	1.09	L.08	1.09	1.11	1.10
Condensate, gms./100 L. In-gas at N.T.P.							
Total	3.78	5.05	5.44	6.27	6.43	4.88	8.05
CH_3OH	1.60	1.66	1.57	1.15	1.27	0.69	0.621
CH_2O	0.078	0.051	0.077	0.07	0.081	0.079	0.076
HCOOH	0.0304	0.0441	0.0314	0.0306	0.0324	0.0249	0.0244
HOH	2.07	3.30	3.75	5.02	5.05	4.09	7.33
% Alcohol In Condensate,	42.2	32.9	29.0	18.5	19.7	14.1	7.72
Carbon Oxidized, gms./100 L.	0.815	0.96	0.939	0.90	0.975	0.821	1.04
Carbon Oxidized, to compounds, gms./ 100 L.	0.642	0.661	0.628	0.469	0.508	0.298	0.270
% of Total Carbon In Oxidized,	1.90	2.48	2.54	2.66	2.90	2.70	3.52
Yields as % of Total Carbon Burned to:							
CH_3OH	74.0	65.3	62.8	48.2	49.2	31.6	22.4
CH_2O	3.82	2.16	3.28	3.13	2.16	3.84	2.94
HCOOH	0.98	1.20	0.87	0.91	0.86	0.90	0.62
Total	78.8	68.66	66.95	52.23	52.22	36.34	25.96
Yields as % of Total Inlet Oxygen to:							
CH_3OH	17.44	12.06	9.96	5.84	6.37	3.09	2.54
CH_2O	0.905	0.399	0.522	0.376	0.563	0.377	0.329
HCOOH	0.46	0.443	0.278	0.215	0.225	0.154	0.138
H_2O	40.0	42.6	42.4	45.2	45.0	32.6	53.1
Total	58.81	55.5	53.16	51.63	52.16	36.21	56.1
% of Total Inlet Oxygen Accounted for:	73.6	76.3	69.0	67.6	66.4	50.4	73.0

Table VII.

Experiment No.	151	146	144	143
Temperature° C.	475	475	475	475
Pressure in Atms.	231	231	231	231
Off-Gas Flow L./Min.	0.84	0.84	0.84	0.84
In-Gas Analysis:				
O_2	3.18	4.42	6.73	8.74
CH_4	79.8	74.3	63.9	54.9
N_2	17.02	21.28	29.37	36.36
Off-Gas Analysis:				
CO_2	0.53	0.63	1.05	1.26
O_2		0.05	0.16	0.13
H_2	0.5	0.55	1.55	2.03
CO			0.11	0.34
CH_4	82.5	77.5	67.2	58.0
N_2	16.47	21.27	29.93	38.24
Volume In-Gas / Volume Off-Gas:	1.05	1.06	1.09	1.09
Condensate, gms./100L. In-gas at N.T.P.				
Total	3.26	4.81	6.61	8.20
CH_3OH	1.34	1.67	1.54	0.694
CH_2O	0.0604	0.0833	0.0965	0.0633
HCOOH	0.0195	0.0447	0.0435	0.0523
H_2O	1.84	3.02	4.93	7.40
% Alcohol In Condensate,	41.0	34.9	23.3	8.46
Carbon Oxidized, gms. /100 L.	0.798	0.99	1.19	1.08
Carbon Oxidized, to compounds gms/100L.	0.531	0.677	0.63	0.30
% of Total Carbon In Oxidized.	1.87	2.49	3.48	3.67
Yields as % of Total Carbon Burned to:				
CH_3OH	62.7	63.2	48.6	24.2
CH_2O	3.03	3.36	3.24	2.30
HCOOH	0.63	1.18	0.95	1.25
Total	66.36	67.64	52.8	27.75
Yields as % of total Inlet Oxygen to:				
CH_3OH	14.75	13.34	8.57	2.80
CH_2O	0.711	0.708	0.665	0.270
HCOOH	0.296	0.494	0.331	0.293
H_2O	36.1	43.1	48.1	52.8
Total	51.86	57.64	57.66	56.16
% of Total Inlet O_2 Accounted for:	67.7	72.2	73.0	72.5

Table VII. A.

Experiment No.	154	153	155	156
Temperature° C.	475	475	475	475
Pressure in Atms.	141	141,	141	141
Off-Gas Flow L./Min.	0.89	0.90	0.89	0.84
In-Gas Analysis:				
O_2	2.77	4.42	6.32	8.35
CH_4	81.6	74.3	65.7	56.6
N_2	15.63	21.28	27.98	35.05
Off-Gas Analysis:				
CO_2	0.53	0.79	1.05	1.23
O_2		0.13	0.11	
H_2	0.55	0.63	1.29	0.63
CO			0.24	
CH_4	84.15	76.8	68.6	59.1
N_2	14.77	21.65	28.71	39.04
Volume In-Gas / Volume Off-Gas:	1.05	1.04	1.09	1.08
Condensate, gms./100L. In-gas at N.T.P.				
Total	2.69	4.29	6.32	8.43
CH_3OH	1.01	1.30	1.35	0.778
CH_2O	0.0657	0.075n	0.10	0.0973
HCOOH	0.0246	0.0409	0.0423	0.0477
H_2O	1.59	2.87	4.83	7.51
% Alcohol In Condensate,	37.6	30.3	21.3	9.22
Carbon Oxidized, gms. /100 L.	0.683	0.967	1.19	0.954
Carbon Oxidized, to compounds gms/100L.	0.414	0.561	0.557	0.344
% of Total Carbon In Oxidized.	1.57	2.43	3.40	3.16
Yields as % of Total Carbon Burned to:				
CH_3OH	55.7	54.0	42.2	30.6
CH_2O	3.80	3.12	3.36	4.07
HCOOH	0.94	1.12	0.93	1.26
Total	60.44	58.24	46.49	35.93
Yields as % of total Inlet Oxygen to:				
CH_3OH	12.76	10.26	7.47	3.26
CH_2O	0.885	0.642	0.592	0.436
HCOOH	0.434	0.449	0.328	0.277
H_2O	35.7	40.4	47.7	63.0
Total	49.78	51.75	56.09	66.97
% of Total Inlet O_2 Accounted for:	68.0	71.8	74.5	80.5

yields of the useful products could not be calculated. This unknown constituent was not removed by potassium hydroxide or fuming sulphuric acid but did not interfere with the operation of the copper oxide tube. Moreover, it interfered with the use of cuprous chloride as a reagent for carbon monoxide. Combustion analysis by two methods on the whole gas gave good checks however. One of the experiments, 425°C., No 91, is included, without of course the yield data which could not be obtained because figures were lacking for carbon monoxide and hydrogen. The results are similar, as far as they go, to those obtained at lower temperatures.

METHANE.

Effect of Inlet Oxygen Concentration.

The effect of inlet oxygen concentration on the survival of the oxygenated products at three pressures, namely, 141, 184 and 231 atmospheres is shown in Figure 15. The experimental results for the above three mentioned pressures are shown in Tables 7A, 6 and 7. Graphs 1 and 2, 3 and 4, 5 and 6, show the yields of the total oxygenated compounds and methyl alcohol, respectively, both based on the percent of the total carbon burned for the previously mentioned pressures. The yields drop off very rapidly at higher oxygen concentrations, more so than with the natural gas-air mixtures. At low oxygen concentrations, the yield passes through a

maximum as the pressure is raised from 141 to 231 atmospheres. This is surprising and contrary to expectations based on Le Chatelier's principle. One would expect a continually increasing yield with increasing pressure. An explanation must be sought in the kinetics of the reaction. At higher oxygen concentrations the yields were decreased to a greater extent at the highest pressure than was true at the lowest pressure. This is well shown in Figure 15 where the yields at oxygen concentrations greater than 8% at 141 atmospheres pressure were greater than those at 231 and 184 atmospheres pressure. The yields at high oxygen concentrations were not changed greatly by pressure changes. However, control of the reaction was difficult and duplicates were not always possible.

Figure 16 shows the percent of alcohol in the condensate and the weight of the condensate in grams per 100 litres of in-gas plotted against the percent of oxygen in the mixture. Graphs 1 and 2, 3 and 4, 5 and 6, refer to 141, 184 and 231 atmospheres pressure, respectively. Graphs 1, 3 and 5 refer to the percent of alcohol in the condensate, Graphs 2, 4 and 6 to the grams of condensate. The percent of alcohol in the condensate dropped nearly linearly with increasing oxygen content in the mixture while the weight of the condensate rose linearly. In other words, the smaller the condensate, the greater was

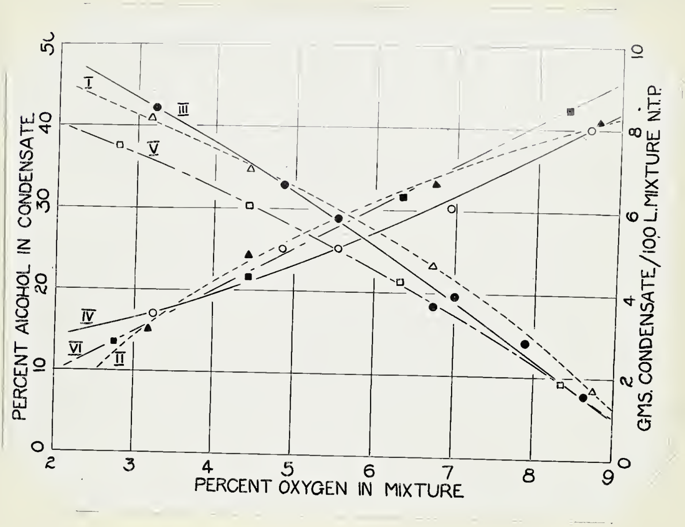
PERCENT ALCOHOL IN CONDENSATE
0
10
20
30
40
50
GMS. CONDENSATE/100 L. MIXTURE N.T.P.
0
2
4
6
8
10
PERCENT OXYGEN IN MIXTURE
2
3
4
5
6
7
8
9
I
II
III
IV
V
VI

Figure 16.

the concentration of alcohol in the liquid products.

The percent of the total carbon oxidized and the weight of the carbon oxidized per 100 litres of in-gas for pressures of 141, 184 and 231 atmospheres is shown by Graphs 4 and 3, 6 and 5, 8 and 7 in Figure 13. At low oxygen concentrations the carbon oxidized rises gradually to a maximum or nearly a constant region near 6% oxygen, the yields, Figure 15, drop rapidly. These graphs for methane are of the same general nature as similar graphs for natural gas, Figures 12 and 13, but differ in not being linear. No definite relationship was obtained between the carbon dioxide and carbon monoxide in the off-gas. Carbon monoxide only appeared at the higher oxygen concentrations and was seldom detected at the lower oxygen concentrations. It is significant of the effect of ethane on the reaction that carbon monoxide appeared in the off-gas in every experiment with natural gas regardless of conditions. The formation of carbon monoxide in the methane experiments only at high oxygen concentrations may be connected with the formation of traces of higher hydrocarbons in many of these experiments. While combustion analysis on the off-gas from the methane experiments showed traces of higher hydrocarbons frequently, the amount appeared to be greater at higher oxygen concentrations.

	Table V111.					Table V111 A.					
Experiment No,	140	139	138	142	143	149	150	147	145	146	148
Temperature° C.	360	390,	390	425	475	390	425	425	475	475	506
Pressure in atms.	231	231	231	231	231	231	231	231	231	231	231
Off-Gas Flow L./min.	0.79	0.80	0.93	0.80	0.84	0.90	0.84	0.88	0.86	0.84	0.87
In-Gas Analysis:											
O_2	8.74	8.54	8.30	8.74	8.74	4.28	4.48	4.42	4.42	4.42	4.42
CH_4	54.9	55.8	56.7	54.9	54.9	74.8	73.8	74.3	74.3	74.3	74.3
N_2	36.36	35.66	35.0	36.36	36.36	20.92	21.72	21.28	21.28	21.28	21.28
Off-Gas Analysis:											
CO_2	2.28	2.08	2.16	1.68	1.26	0.84	0.79	0.83	0.73	0.63	0.73
O_2	0.47	0.16	0.13	0.26	0.13		0.11		0.13	0.05	0.05
H_2	0.47	0.63	0.61	1.34	2.03	0.37	0.50	0.53	0.89	0.55	0.82
CO		0.16	0.10	0.29	0.34						
CH_4	58.7	58.7	59.35	58.4	58.0	77.8	77.8	77.4	77.2	77.5	77.1
N_2	38.08	38.27	37.65	38.03	38.24	20.99	20.8	21.24	21.02	21.27	21.3
Volume In-Gas / Volume Off-Gas:	1.14	1.12	1.11	1.12	1.09	1.06	1.08	1.06	1.07	1.06	1.06
Condensate, gms./100L: In-gas at N.T.P.											
Total	8.55	8.69	8.44	8.39	8.20	4.84	4.73	4.79	4.70	4.81	4.48
CH_3OH	1.74	1.91	1.85	1.37	0.694	1.74	1.72	1.63	1.66	1.67	1.42
CH_2O	0.116	0.114	0.104	0.0908	0.0633	0.109	0.081	0.078	0.0743	0.0833	0.0769
HCOOH	0.0707	0.0407	0.0411	0.0596	0.0523	0.0273	0.026	0.0412	0.0454	0.0447	0.0361
H_2O	6.63	6.63	6.43	6.87	7.40	2.96	2.90	3.04	2.92	3.02	2.94
% Alcohol, Condensate	20.4	22.0	21.9	16.4	8.46	35.8	36.4	34.0	35.3	34.9	31.8
Carbon Oxidized, gms. / 100 L.	1.80	1.84	1.83	1.51	1.08	1.13	1.078	1.073	1.036	0.99	0.95
Carbon Oxidized, to compounds, gms/ 100L.	0.731	0.773	0.745	0.567	0.30	0.703	0.698	0.645	0.672	0.677	0.575
% of Total Carbon In Oxidized,	6.13	6.18	6.05	5.13	3.67	2.81	2.73	2.70	2.61	2.49	2.39
Yields as% of Total Carbon Burned to:											
CH_3OH	37.0	38.8	37.8	34.2	24.2	58:0	60.2	57.2	60.4	63.2	56.3
CH_2O	2.58	2.48	2.26	2.42	2.30	3.85	3.02	2.91	3.16	3.36	3.24
HCOOH	1.03	0.58	0.59,	1.03	1.25	0.62	0.63	0.99	1.15	1.18	0.99
Total	41.61	41.86	40.65	37.65	27.75	62.47	63.85	61.10	64.71	67.64	60.53
Yields as % of Total Inlet Oxygen to:											
CH_3OH	7.00	7.80	7.80	5.51	3.80	14.2	13.46	12.9	13.2	13.34	11.33
CH_2O	0.498	0.498	0.468	0.388	0.27	0.95	0.68	0.652	0.637	0.708	0.655
HCOOH	0.396	0.232	0.242	0.333	0.293	0.31	0.286	0.455	0.50	0.494	0.40
H_2O	47.3	48.3	48.3	49.0	52.8	43.2	40.3	43.1	41.3	43.1	41.7
Total	45.19	56.83	56.81	55.23	56.16	58.66	54.73	57.11	55.64	57.64	54.09
% of Total Inlet O_2 Accounted for:	82.8	81.0	82.2	76.5	72.5	77.8	73.2	73.3	74.5	72.2	73.0

The total oxygen conversion to the liquid products was not constant and it varied erratically with inlet oxygen concentration at 184 atmospheres pressure. However, at pressures of 141 and 231 atmospheres the oxygen conversion to liquid products rose slightly with an increase in the inlet oxygen concentration. It will be noticed that the oxygen recoveries are always less than 100%, frequently by very large amounts. This is generally true of all methane experiments and has not been accounted for in a satisfactory manner.

Effect of Temperature.

The variation of yields of the total oxygenated compounds and methyl alcohol based on the total carbon burned with temperature and pressures of 231 and 184 atmospheres at 4.42% and 4.85% inlet oxygen are shown in Figure 17 and in Tables 8A and 10. Graphs 1 and 2, 3 and 4, in Figure 17 show the yields of the total oxygenated compounds and methyl alcohol at 184 and 231 atmospheres pressure, respectively.

The optimum operating temperature was approximately the same at both pressures being in the neighborhood of 460°C. The graphs are somewhat conventional but do represent generally the results of many experiments at low temperatures, 400°C. or less, where duplicates were very difficult to obtain. The

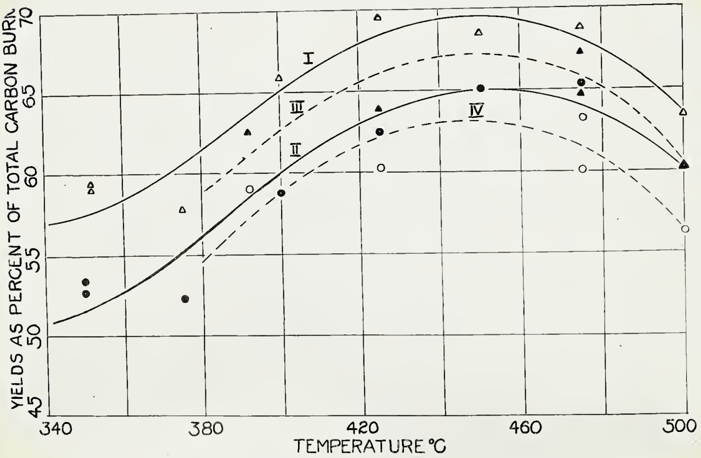
YIELDS AS PERCENT OF TOTAL CARBON BURN
45
50
55
60
65
70
340
380
420
460
500
TEMPERATURE °C
I
II
III
IV

Figure 17.

Table 1X.

Experiment No,	123	126	125	134	127	135	130	133	132	136	137
Temperature°C.	340	350	360	360	360	375	390	390	390	425	475
Pressure in atms.	184	184	184	184	184	184	184	184	184	184	184
Off-Gas Flow L./min.	0.84	0.84	0.62	0.79,	0.99	0.81	0.82	0.85	0.85	0.78	0.78
In-Gas Analysis:											
O_2	8.64	8.64	8.64	8.70	8.64	8.60	8.71	8.68	8.54	8.74	8.63
CH_4	55.4	55.4	55.4	55.0	55.4	55.5	55.0	55.2	55.8	54.9	55.4
N_2	35.96	35.96	35.96	36.3	35.96	35.9	36.29	36.12	35.66	36.36	35.97
Off-Gas Analysis:											
CO_2	0.50	2.00	2.16	2.52	1.92	2.42	2.09	2.52	2.52	1.79	1.37
O_2	8.15	0.11	0.32	0.11	0.16	0.11	0.05		0.11	0.21	0.13
H_2	0.24	1.16	0.71	0.68	1.16	0.58	0.82	0.61	0.71	1.16	1.84
CO		0.63	0.63	0.11	0.42	0.11	0.18	0.11	0.11	0.21	0.21
CH_4	56.1	58.55	58.1	58.1	59.5	57.9,	59.1	58.3	58.1	58.0	58.6
N_2	35.01	37.55	38.08	38.48	36.84	38.88	37.76	38.46	38.45	38.63	37.85
Volume In-Gas Volume Off-Gas:	1.02	1.10	1.10	1.13	1.11	1.11	1.11	1.13	1.11	1.11	1.10
Condensate, gms./100L. In-gas at N.T.P.											
Total		8.53	8.71	7.95	8.48	8.27	8.75	8.34	8.35	8.39	8.05
CH_3OH		1.54	1.75	1.48	1.58	1.59	1.76	1.63	1.61	1.08	0.621
CH_2O		0.125	0.150	0.130	0.121	0.113	0.118	0.111	0.113	0.112	0.763
HCOOH		0.0388	0.0479	0.0392	0.0463	0.0367	0.0432	0.0219	0.0306	0.0286	0.0244
H_2O		6.83	6.76	6.30	6.73	6.53	6.83	6.58	6.60	7.17	7.33
% Alcohol In Condensate,		18.1	20.1	18.6	18.6	19.2	20.2	19.5	19.3	12.8	7.72
Carbon Oxidized, gms. /100 L.	0.0262	1.92	2.09	1.84	1.78	1.86	1.81	1.90	1.92	1.42	1.04
Carbon Oxidized, to compounds, gms,/ 100 L.		0.642	0.73	0.621	0.655	0.637	0.721	0.646	0.646	0.456	0.27
% of Total Carbon In Oxidized,	0.883	6.49	7.06	6.27	6.00	6.25	6.15	6.42	6.41	4.84	3.52
Yields as % of Total Carbon Burned to:											
CH_3OH		30.2	31.6	30.3	33.4	31.4	36.8	32.2	31.7	28.5	22.4
CH_2O		2.60	2.86	2.81	2.72	2.41	2.60	1.54	1.54	3.16	2.94
HCOOH		0.53	0.60	0.56	0.68	0.49	0.62	0.30	0.40	0.54	0.62
Total		33.3	35.06	33.67	36.8	34.3	40.02	34.04	33.64	32.2	25.96
Yields as % of Total Inlet Oxygen to:											
CH_3OH		6.28	7.13	5.98	6.42	6.50	7.11	6.58	6.65	4.33	2.54
CH_2O		0.542	0.647	0.56	0.523	0.639	0.504	0.478	0.495	0.629	0.329
HCOOH		0.219	0.272	0.22	0.26	0.208	0.242	0.127	0.181	0.162	0.138
H_2O		49.5	48.8	45.3	48.7	47.3	49.2	47.4	48.2	51.3	53.1
Total		56.54	56.84	52.06	55.9	56.65	57.06	54.59	55.53	56.42	56.1
% of Total Inlet Oxygen Accounted for:	97.0	81.7	86.3	79.5	79.6	81.6	80.0	81.0	83.7	79.2	73.0

Table X.

Experiment No.	94	95	96	97	98	99	100	101
Temperature °C.	350	375	400	425	450	475	500	350
Pressure in Atms.	184	184	184	184	184	184	184	184
Off-Gas Flow L./Min.	0.73	0.70	0.78	0.66	0.79	0.80	0.74	0.74
In-Gas Analysis:								
O_2	4.86	4.96	5.03	4.85	4.85	4.85n	4.85	4.85
CH_4	72.9	72.0	72.6	73.0	73.0	72.5	72.5	72.5
N_2	22.24	23.04	22.36	22.15	22.15	22.65	22.65	22.65
Off-Gas Analysis:								
CO_2	0.95	0.95	0.74	0.65	0.63	0.58	0.63	0.97
O_2	0.26	0.21	0.53	0.24	0.16	0.47	0.26	0.26
H_2	0.24	0.19	0.16	0.23	0.21	0.26	0.21	0.16
CO								
CH_4	75.45	74.8	74.2	75.4	75.5	74.9	75.2	75.3
N_2	23.1	23.85	24.37	23.48	23.39	23.79	23.7	23.31
Volume In-Gas / Volume Off-Gas:	1.05	1.07	1.05	1.04	1.04	1.04	1.04	1.05
Condensate, gms./100 L. In-gas at N.T.P.								
Total	5.00	4.78	5.17	5.38	5.25	5.05	4.75	5.26
CH_3OH	1.67	1.57	1.73	1.82	1.76	1.66	1.40	1.74
CH_2O	0.134	0.115	0.158	0.139	0.0586	0.0508	0.0474	0.148
HCOOH	0.084	0.0726	0.0604	0.0814	0.0441	0.0441	0.0305	0.0505
H_2O	3.12	3.02	3.22	3.34	3.39	3.30	3.27	3.32
% Alcohol In Condensate,	33.3	32.9	33.4	33.9	33.6	32.9	29.6	33.1
Carbon Oxidized, gms./100L:	1.18	1.13	1.11	1.09	1.02	0.96	0.878	1.22
Carbon Oxidized, to compounds, gms,/ 100 L.	0.702	0.657	0.732	0.763	0.698	0.661	0.557	0.727
% of Total Carbon In Oxidized,	3.03	2.93	2.85	2.80	2.61	2.48	2.26	3.14
Yields as % of Total Carbon Burned to:								
CH_3OH	52.7	52.2	58.8	62.5	65.1	65.3	60.2	53.4
CH_2O	4.53	4.08	5.07	5.07	2.26	2.16	2.16	4.85
HCOOH	1.85	1.67	1.42	1.94	1.12	1.20	0.93	1.08
Total	59.08	57.95	65.92	69.51	68.48	68.66	63.29	59.33
Yields as % of Total Inlet Oxygen to:								
CH_3OH	11.9	11.12	11.24	13.20	12.73	12.06	10.10	12.58
CH_2O	1.02	0.873	1.172	1.074	0.449	0.399	0.366	1.146
HCOOH	0.837	0.715	0.584	0.818	0.440	0.443	0.307	0.507
H_2O	39.7	38.1	39.8	43.0	43.7	42.6	41.8	42.8
Total	53.46	50.81	53.8	58.09	57.32	55.5	52.57	57.14
% of Total Inlet Oxygen Accounted for:	79.0	72.6	77.7	75.3	72.8	76.3	70.2	81.2

exothermic nature of the reaction interfer~~r~~ed particularly with the temperature control at lower temperatures. It was peculiar that the reaction was easily controlled at 350°C. but was highly erratic at 375°C.

The stability of the catalyst was shown in experiments 94 and 101, the catalyst having been used at all temperatures up to 500°C. between these experiments without affecting apparently its activity. At higher temperatures and 184 atmospheres pressure no difficulty was found in obtaining satisfactory duplicates. However, at 231 atmospheres pressure duplicate experiments would not check. This is well shown by experiments 145 and 146 at 475°C. and experiments 150 and 147 at 425°C. in Table 8A. The temperature control in all these experiments was good and no difficulty was had with the other variables concerned. It appears that the catalyst was changing its surface at the time or else impurities were entering the reacting system.

The effect of temperature on the yields at 184 and 231 atmospheres pressure at an oxygen concentration of 8.7% is shown in Figure 18. The data are from Tables 8 and 9. The optimum temperature of operation was in the neighborhood of 390°C. An increase in pressure raised the optimum working temperature very slightly. The yields at both pressures dropped slowly with an increase in

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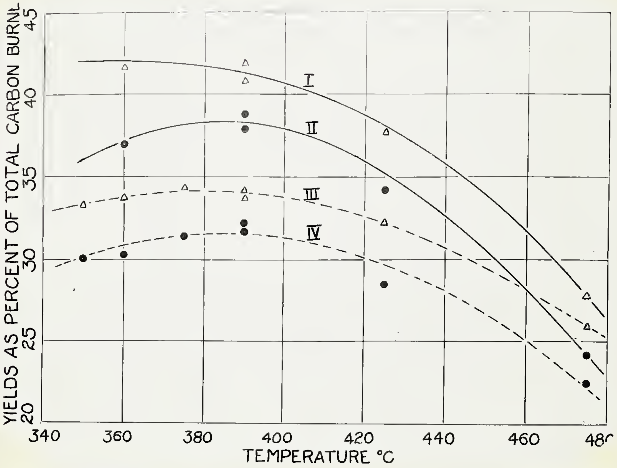

YIELDS AS PERCENT OF TOTAL CARBON BURNE
20
25
30
35
40
45
340
360
380
400
420
440
460
48
TEMPERATURE °C
I
II
III
IV

Figure 18.

temperature.

The weight of the condensate for any one pressure and mixture remained practically constant with a change in temperature. In some of the experiments an increase in temperature above the optimum working value decreased the weight of the liquid products. The percent of alcohol in the condensate did not change appreciably with temperature. In all these experiments there was a rough inverse correlation between weight and composition of condensate as shown, for example, in Figure 16.

The percent of the total carbon burned decreased with an increase in temperature. This effect is shown in Table 10 and may be accounted for by the increase in space velocity over the catalyst with rising temperature.

A rise in temperature did not result in significant changes in the off-gas composition nor did it result in carbon monoxide formation. However, at high inlet oxygen concentrations carbon monoxide, in quantities as high as 0.63% in the off-gas, was obtained. Tables 9 and 8 show the variation of carbon monoxide in the off-gas for pressures of 184 and 231 atmospheres.

No very clear relationship existed between the yield of the liquid products based on the total inlet oxygen and the temperature of operation. A rise to a maximum at 425 to 450°C. is indicated.

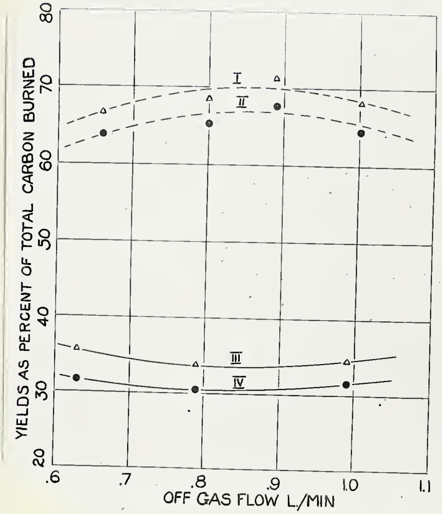

YIELDS AS PERCENT OF TOTAL CARBON BURNED
80
70
60
50
40
30
20
.6
.7
.8
.9
1.0
1.1
OFF GAS FLOW L/MIN
I
II
III
IV

Figure 19.

	Table Xl.				Table Xl A.			
Experiment No,	108	99	110	111	105	106	104	103
Temperature°C.	475	475	475	475	475b	475	475	475
Pressure in atms.	184	184	184	184	184	184	184	184
Off-Gas Flow L./Min.	0.66	0.80	0.89	1.03	0.47	0.66	0.73	0.91
In-Gas Analysis:								
O_2	4.85	4.85	4.87	4.95	5.05	4.95	4.45	4.85
CH_4	72.7	72.5	72.7	72.3	72.6	72.3	74.2	72.5
N_2	22.45	22.65	22.43	22.75	22.35	22.75	21.35	22.65
Off-Gas Analysis:								
CO_2	0.63	0.58	0.53	0.63	0.74	0.74	0.74	0.71
O_2	0.31	0.47	0.21	0.16	0.42	0.16	0.11	0.18
H_2	0.11	0.26	0.26	0.11	0.26	0.16	0.11	0.32
CH_4	75.0	74.9	75.5	75.2	73.3	74.9	77.0	75.2
N_2	23.95	23.79	23.5	23.8	25.28	24.04	22.04	23.59
Volume In-Gas								
Volume Off-Gas:	1.05	1.04	1.05	1.06	1.04	1.06	1.06	1.05
Condensate, gms./100 L. In-gas at N.T.P								
Total	5.06	5.05	5.25	5.28	5.10	5.08	4.66	5.01
CH_3OH	1.64	1.66	1.70	1.69	1.45	1.46	1.46	1.50
CH_2O	0.0472	0.0568	0:0607	0.0698	0.0423	0.0417	0.0462	0.0832
HCOOH	0.0404	0.0441	0.0337	0.0299	0.0618	0.0370	0.0319	0.0510
H_2O	3.33	3.30	3.46	3.49	3.55	3.54	3.12	3.38
% Alcohol In Condensate,	32.4	32.9	32.4	32.1	28.4	28.7	31.4	30.0
Carbon Oxidized, gms. / 100 L.	0.967	0.96	0.945	0.99	0.97	0.946	0.947	0.973
Carbon Oxidized, to Compounds, gms,/ 100 L.	0.646	0.661	0.673	0.675	0.587	0.573	0.575	0.611
% of Total Carbon In Oxidized,	2.48	2.48	2.42	2.56	2.50	2.45	2.39	2.51
Yields as % of Total Carbon Burned to:								
CH_3OH	63.8	65.3	67.8	64.4	57.3	57.8	57.9	58.0
CH_2O	1.95	2.16	2.57	2.82	1.74	1.76	1.96	3.42
HCOOH	1.09	1.20	0.96	0.79	1.67	1.02	0.88	1.37
Total	66.84	68.66	71.33	68.01	60.71	60.58	60.74	62.79
Yields as % of Total Inlet Oxygen to:								
CH_3OH	11.85	12.06	12.28	12.02	10.08	10.36	11.52	10.82
CH_2O	0.366	0.399	0.466	0.529	0.314	0.316	0.389	0.639
HCOOH	0.405	0.443	0.338	0.295	0.597	0.365	0.350	0.512
H_2O	42.9	42.6	44.3	44.2	43.9	44.7	43.9	43.4
Total	55.52	55.5	57.38	57.04	54.89	55.74	56.16	55.37
% of Total Inlet Oxygen Accounted for:	74.0	76.3	72.0	72.0	77.0	73.0	74.0	75.0

Effect of Rate of Flow.

The effect of rate of flow on the survival of the useful oxidation products at 360°C. and 475°C. with an 8.6% and 4.85% inlet oxygen concentration at 184 atmospheres pressure is shown in Figure 19. The results of the experiments are shown in Table 9, including experiments 125, 134 and 127, and Table 11. Graphs 1 and 2, 3 and 4 in Figure 19 show the yield of the total oxygenated products and methyl alcohol at 4.85 and 8.6 percent oxygen in the mixture. Increase in the rate of flow in the range investigated was of little effect on the yields of the useful products. A maximum appears in one case and a minimum in the other but they are barely outside the variation between duplicate experiments. The same result was not obtained in the natural gas-air experiments in which the yields to useful products decreased appreciably with the rate of off-gas flow. Table 11A. shows the effect of rate of flow on the yield when the catalyst was poisoned. While very much lower, the yields are practically independent of rate of flow.

The amount of inlet carbon burned at 8.64% and 4.85% inlet oxygen concentration did not vary a great deal with the rate of flow and was in the neighborhood of 6.5% and 2.5%, respectively. The oxygen conversion to the liquid products and the oxygen recovery were not

Table X11.

Experiment No,	157	158	159	160	161
Temperature°C.	475	475	475	475	475
Pressure In Atms.	141	141	141	141	141
Off-Gas Flow L./Min.	0.85	0.88	0.84	0.90	0.88
In-Gas Analysis:					
O_2	8.57	8.85	8.68	4.35	4.52
CH_4	55.7	54.5	55.2	73.85	73.8
N_2	35.73	36.65	36.12	21.15	21.68
Off-Gas Analysis:					
CO_2	0.97	1.08	2.02	1.05	1.00
O_2			0.11	0.13	0.05
H_2	0.76	0.53	0.97	0.90	0.87
CO			0.11		
CH_4	60.3	58.9	58.3	77.6	77.5
N_2	37.97	39.49	38.49	20.32	20.58
Volume In-Gas / Volume Off-Gas:	1.10	1.10	1.09	1.00	1.06
Condensate, gms./ 100L. In-gas at N.T.P.					
Total	7.95	8.39	7.99	4.09	4.08
CH_3OH	0.231	0.436	1.23	1.07	1.20
CH_2O	0.0427	0.0705	0.0971	0.0947	0.091
$HCOOH$	0.0375	0.0654	0.0586	0.0293	0.0193
H_2O	7.63	7.82	6.60	2.90	2.77
% Alcohol In Condensate,	2.9	5.2	15.4	26.2	29.2
Carbon Oxidized, gms. / 100 L.	0.583	0.734	1.56	1.01	0.994
Carbon Oxidized to Compounds, gms,/ 100 L.	0.114	0.209	0.518	0.449	0.487
% of Total Carbon In Oxidized,	1.96	2.52	5.30	2.39	2.51
Yields as % of Total Carbon Burned to:					
CH_3OH	14.9	22.4	29.6	39.8	45.0
CH_2O	2.91	3.84	2.48	3.78	3.66
$HCOOH$	1.65	2.31	0.97	0.77	0.51
Total	19.46	28.55	33.05	43.35	49.17
Yields as % of Total Inlet Oxygen to:					
CH_3OH	0.945	1.74	4.99	8.63	9.17
CH_2O	0.186	0.301	0.556	0.813	0.752
$HCOOH$	0.215	0.362	0.329	0.329	0.206
H_2O	55.7	55.3	47.5	41.5	38.2
Total	57.05	57.7	53.37	51.27	48.33
% of Total Inlet Oxygen Accounted for:	67.3	69.0	78:0	78.2	70.0

related in any way to the off-gas flow rate. The weight and composition of the condensate did not change appreciably with the rate of flow. Alcohol was present to the extent of 19% by weight of the condensate at the higher oxygen concentration used and 32.5% at the lower.

The rate of flow as given refers of course to the whole gas. Changing the oxygen concentration changes the actual rate of flow and care has to be taken in making comparisons between the behavior of different gas mixtures. The small effect of changing the rate of flow,however,permits the conclusions that rate of flow in the range used is of little consequence.

Other Catalysts.

Tables 12 and 13 show experiments made with an empty reactor and with the following catalysts-copper, glass, enduro steel and silver. No definite results were obtained with the empty reactor because duplicate experiments would not check. The yields in duplicate experiments varied considerably as did also the weight of the condensate and the percent of the total carbon oxidized. The same result was obtained with high and low concentrations of oxygen in the mixture. Because of the increased volume of the autoclave due to the absence of the catalyst the space velocity was very small and this no doubt was responsible in part for the erratic results

Table X111.

Experiment No,	115	114	1	153	162	163	164
Catalyst.	Copper	glass		Copper	Enduro	Enduro	Silver
Temperature°C.	475	475		475	475	475	475
Pressure in atms.	184	184		141	141	141	141
Off-Gas Flow L./Min.	0.84	0.85		0.90	0.77	0.88	0.89
In-Gas Analysis:							
O_2	3.22	3.16		4.42	4.45	4.42	4.22
CH_4	80.0	80.2		74.3	74.0	74.3	74.3
N_2	16.78	16.64		21.28	21.55	21.28	21.28
Off-Gas Analysis:							
CO_2	0.34	0.37		0.79	1.08	1.05	0.68
O_2	0.16	0.18		0.13			0.18
H_2	0.26			0.63	0.63	0.82	0.66
CO							0.05
CH_4	81.4	82.0		76.8	78.0	78.0	77.9
N_2	17.84	17.34		21.65	20.29	20.13	20.53
$\frac{\text{Volume In-Gas}}{\text{Volume Off-Gas}}$:	1.04	1.04		1.04	1.07	1.06	1.07
Condensate, gms./ 100 L. In-gas at N.T.P.							
Total.	3.78	3.91		4.29	3.82	3.65	4.51
CH_3OH	1.60	1.71		1.30	1.13	1.03	1.25
CH_2O	0:078	0.0644		0.075	0.0515	0.0502	0.136
HCOOH	0.0304	0.0305		0.0409	0.0419	0.0422	0.0254
H_2O	2.07	2.10		2.87	2.60	2.53	3.10
% Alcohol In Condensate,	42.2	44.0		30.3	29.6	28.2	27.8
Carbon Oxidized, gms. / 100 L.	0.815	0.867		0.967	1.00	0.947	0.902
Carbon Oxidized to compounds, gms,/ 100 L.	0.642	0.678		0.561	0.458	0.419	0.535
% of Total Carbon In Oxidized,	1.90	2.02		2.43	2.50	2.38	2.27
Yields as % of Total Carbon Burned to:							
CH_3OH	74.0	74.2		54.0	42.5	41.1	52.3
CH_2O	3.82	2.97		3.12	2.08	2.14	6.04
HCOOH	0.98	0.92		1.12	1.09	1.15	0.74
Total	78.8	78.09		58.24	45.67	44.39	59.08
Yields as % of Total Inlet Oxygen to:							
CH_3OH	17.44	19.0		10.26	8.95	8.20	10.43
CH_2O	0.905	0.761		0.642	0.433	0.428	1.21
HCOOH	0.46	0.47		0.449	0.458	0.466	0.294
H_2O	40.0	41.5		40.4	36.6	35.9	46.0
Total	58.81	61.73		51.75	46.44	44.99	57.93
% of Total Inlet Oxygen Accounted for:	73.6	78.5		71.8	69.0	67.5	77.5

obtained. The possibility of uncontrolled reaction for relatively long periods of time and the uncertainty of the temperature in the gas mixture are contributing factors. These results with the empty autoclave were of prime importance. They showed, that in order to get controlled oxidation, first, the space velocity must be above a certain minimum value and second, a good heat conductor to maintain uniform temperature throughout the reacting gases was necessary. It may be true also that the reactions of value are surface reactions, requiring a surface that is under fair temperature control to dissipate the heat of these exothermic reactions. Previous work (9) demonstrated this same point, that large gas spaces were detrimental.

The effect of different catalysts on the oxidation of methane is shown in Table 13. As regards the yields to useful products copper, glass and silver were equally good. Silver, however, tended to produce more formaldehyde than either copper or glass. By comparing experiments 153 and 164 it is seen that silver produces about twice as much formaldehyde as copper when used under identically the same conditions. However, the total amount of carbon burned in each case was the same. Enduro steel was a very poor catalyst since controlled combustion could not be obtained with its use and consequently, very low yields resulted. All the catalysts

used did not have the same volume and so the space velocity would be different in each case. Comparisons as regards yields cannot be overstressed because of this fact. For example, the silver used had a much smaller volume than the copper with the result that the mixture was in contact with the silver for a longer period of time. This would account, no doubt, for the larger amount of formaldehyde surviving with the silver, more opportunity for the oxidation of the alcohol occurring.

The effectiveness of glass as a catalyst was unexpected. Glass is not a good conductor of heat and the temperature control should be poor. It is concluded that the reactions on glass follow a different course and are much slower than on metals so that the heat is liberated more slowly. One also may suggest that all the reactions took place on the copper-plated interior walls of the reactor, the function of the glass being merely the suppression of undesirable gas phase reactions such as occurred with the empty autoclave.

The ineffectiveness of the Ni-Cr-Fe alloy, Enduro steel, may be attributed to the metals of which it is composed. They promote complete oxidation, and further, all form oxides that are not easily reduced. Copper and silver form readily reducible oxides and it is beleived that this property has a great deal to do with

their effectiveness in the reaction. Visual inspection of the copper catalyst after use suggests very strongly the presence of cuprous oxide on its surface. The enduro steel catalyst showed little change after use.

Oxygen Balances:-

The oxygen balance did not check, the recovery in gaseous and liquid products of the reactions ranging from 60% to 146% in different experiments. Recoveries over 100% were obtained only with natural gas. The discrepencies were very great in some experiments and there was no definite relationship between the oxygen accounted for and the different variables investigated. Since a deficiency of oxygen was always obtained in the methane-air experiments a series of experiments were made to trace the missing oxygen. The first possibility tested was the retention of oxygen by the catalyst, an almost certain occurrence on a small scale but unlikely to explain tha large losses observed. It was with this point in view that glass was used as a catalyst, a catalyst which would absorb no oxygen. However, the results obtained were similar to those with copper a recovery of only 78.5% of the oxygen being obtained. Again the walls of the reactor might absorb some of the oxygen at the operating temperatures that were used. This possibility was examined by isolating the reacting system at the completion of an experiment and after

allowing the whole to reach room temperature, samples of the mixture were withdrawn for analysis. The analysis of the mixture showed it to have about the same composition as the off-gas obtained in the normal experiment. The oxygen content was however a little high, explicable since all the gas in the high pressure system was not passed through the catalyst chamber. A further possibility investigated was the formation of gaseous oxygen compounds which would not be determined in the off-gas analysis. Consequently the off-gas in one of the experiments was passed through a quartz tube heated to 1100°C. at which temperature methane and any higher hydrocarbons would be cracked while any oxygenated carbon compounds being less stable would decompose certainly to carbon, carbon monoxide, carbon dioxide and water. A sample of the cracked off-gas was analyzed and it was shown to have the same oxygen content as the original gas before heating. The methods of analysis of condensates were confirmed on pure substances and further, whole samples were analyzed for carbon and hydrogen by the methods of ultimate organic analysis with excellent agreement between the methods. Impossible as it may appear, nevertheless the fact remains that all the oxygen entering the reactor did not come out in the liquid and gaseous products and it appears unlikely that the lost oxygen remained in the catalyst. No solid

compounds formed in the reactor or in the system in any case. The recovery of surplus oxygen in the natural gas experiments is just as puzzling. One is forced to the conclusion that failure to balance oxygen is connected with the reactor, probably in combination with the copper, and it is hoped that further tests will clear up the point. The quantity of oxygen lost, and for that matter the quantities gained in the natural gas experiments, are so large in many cases, however, as to cast some doubt on absorption by metal as an explanation. Weizevich and Frolich (31) in their experiments on the oxidation of natural gas and methane only accounted for 70% of the in-going oxygen. With experiments on the oxidation of propane only about 40% of the oxygen was recovered in the products. They offer no explanation but apparently must have had the same difficulty in accounting for all the oxygen as experienced here.

Discussion.

In the previous sections the results have been presented together with some discussion of the salient features. In general it may be concluded that the yield of useful products depends primarily on oxygen concentration and temperature. They depend to a lesser extent on the pressure of operation and only slightly on space velocity at least within the range used. Catalysts are of importance, apparently fulfilling two

functions. A catalyst should provide a suitable reaction surface and one satisfactory surface appears to be that of a metal easily oxidized and reduced. Further, the catalyst must fulfill either or both functions of providing uniform temperature distribution and reducing the free gas space to a minimum. Gas phase reactions and uncontrolled temperature are both detrimental. The weight of condensates varied little from experiment to experiment for any one oxygen concentration but did of course decrease as the oxygen content of the in-gas decreased. The alcohol content of the condensate paralleled the yield, the water content increasing as the yield went down.

The general features of the results may be explained reasonably well by a mechanism involving features of Bone's Hydroxylation theory (3) and Norrish's Chain theory (27). Obvious confirmation of the general truth of Bone's theory lies in the production of large amounts of methyl alcohol together with formaldehyde and formic acid in smaller amounts. The dependence of yield on oxygen concentration and the fact that a high pressure is necessary for the production of useful products are details explicable on this theory. Finally, tests for peroxides were always negative suggesting that the peroxide theory is not applicable.

Bone's theory does not offer a satisfactory explanation, however, for many observations regarding

the minor products of the reaction and the kinetics of the reaction. It is believed that Norrish's theory clears up many of these points and the following theory, combining aspects of both, is presented.

The primary reactions suggested are two, a surface reaction between methane and oxygen and a homogeneous gas phase reaction between methane and oxygen. Both reactions require activated oxygen; in the first, the oxygen may be absorbed on the catalyst surface or combined with the catalyst, for example as cuprous oxide, and in the second, the oxygen may be as activated of in the atomic form. The source of the atomic or activated gaseous oxygen will be discussed later. We may write the surface reaction as:-

$$CH_4 + O_S \longrightarrow CH_3OH \qquad (1)$$

or $$CH_4 + Cu_2O \longrightarrow CH_3OH + 2Cu.$$

The methanol may survive or proceed to formaldehyde or formic acid by Bone's mechanism through further oxidation. This reaction is required by Bone as the first stage in the oxidation of methane and moreover it is admitted by Norrish as a reaction that occurs; in the latter theory it plays the role of a chain breaker. The homogeneous reaction may be taken from Norrish as:-

$$CH_4 + O^+ \longrightarrow CH_2: + H_2O \qquad (2)$$

$$CH_2: + O_2 \longrightarrow CH_2O + O^+ \qquad (3)$$

A chain reaction which is broken by (1) above. We may

also postulate the occurrence of the reactions:-

$$n\ CH_2: \longrightarrow (CH_2)_n \qquad (4)$$

$$CH_2O \longrightarrow CO + H_2 \qquad (5)$$

or

$$CH_2O + 1/2\ O_2 \longrightarrow CO + H_2O \qquad (6)$$

all of which are known to occur in other work.

Low oxygen concentrations favor methanol production and one may conclude this from reaction (1) above. This is only to be expected since with a limited supply, and a good catalyst, most of the oxygen in the reactive form will be on the catalyst. The methanol formed will survive in large part; to undergo further oxidation it would have to compete with the much larger quantity of methane present for oxygen. However, at high oxygen concentrations a considerable amount of activated oxygen may be expected in the gas phase. Methanol might be expected to oxidize further, the whole Bone series of reactions moving further toward carbon monoxide, carbon dioxide and water.

A further and probably more important effect of high oxygen concentrations will be the promotion of the reactions in Norrish's theory, (2) and (3) above. These are homogeneous reactions and should be promoted by increased oxygen concentration in the gas phase whereas the reaction (1) above is heterogeneous and relatively independent of oxygen concentration once

the catalyst surface is covered. Hence one might expect an increased production of aldehydes and higher hydrocarbons, reaction (4), at high oxygen concentrations. However, as is well known, aldehydes are very reactive compared to alcohols and hydrocarbons and little would survive. Rather an increased production of carbon monoxide, carbon dioxide and water would result. In the methane experiments, the reduction in methanol yield, the production of carbon monoxide and the increased traces of higher hydrocarbons only at high oxygen concentrations is explicable on this basis. At low oxygen concentrations, methanol is the primary product and the amount of aldehyde formed is so small as to give no carbon monoxide. The reactions (3) and (4) are nearly if not entirely suppressed under these conditions. The occurrence of explosions at the highest oxygen concentration used is readily explained on Norrish's theory through the formation of aldehydes in large amounts. The reactive nature of the aldehyde, compared to methanol and methane would account for the explosions.

Summarizing, it is proposed that two primary reactions occur, (1) and (2) above, the first being heterogeneous and desirable leading to the Bone mechanism of oxidation, the second being a homogeneous chain reaction yielding formaldehyde and gases but no methanol and so undesirable. The relative proportion

of each in the whole reaction depends mainly upon oxygen concentration, the proportion of the second increasing with increasing oxygen concentration.

Increasing the pressure of the reactants would affect the two reactions. With increasing pressure, reaction (1) should be promoted through increased velocity and shift in equilibrium. Moreover, further reactions in the Bone series would be suppressed. However, the pressure of methane only would be effective, the effect of increased oxygen pressure being small on the assumption that the catalyst is practically saturated with oxygen at all concentrations. Reactions (2) and (3) will be increased in velocity by increase in pressure or concentration of both methane and oxygen with oxygen probably the most important reagent. These are detrimental reactions. The observed results at low oxygen concentrations that there is a maximum in the pressure-yield relation follows on the above theory. As the pressure is raised at constant oxygen concentration, reaction,(1), the predominating reaction, and at the same time reactions (2) and (3) are promoted. It is conceivable that the velocity of reactions (2) and (3) increase more rapidly with pressure than reaction (1), the velocity depending on two reactants in the former

case as against one reactant in the latter. Ultimately, and presumably above 184 atmospheres pressure for the experiments in question, reactions (2) and (3) predominate and the yield of methanol falls. As the oxygen concentration in the gas is increased, the effect of pressure should change, reactions (2) and (3) being favored at the expense of reaction (1) and ultimately a decrease in pressure should favor reaction (1). This was found to be the case (Figure 15) at 8-9% oxygen where the minimum pressure of 141 atmospheres gave the highest yield of methanol.

The effect of temperature is more or less obvious. Once the ignition temperature is reached, the effect of increased temperature is to increase the velocity of all reactions, the secondary reactions in both mechanisms as well as the primary. At sufficiently high temperatures depending on the oxygen concentration the oxidation and decomposition of the primary products methanol and formaldehyde to carbon monoxide, carbon dioxide and water will be so extensive as to result in a decrease in yield. This has been observed, the optimum temperature being nearly independent of pressure but dependent on oxygen concentration.

The effect of space velocity on the reactions is not so clear. One might say at first sight that increasing rate of flow should result in increased yields

of the primary products but such was not the case. The conclusion to be drawn is that within the range of space velocity used, the reactions were always complete or there was no time for further reaction. Neither methanol or formaldehyde are stable with respect to their decomposition products carbon monoxide, and hydrogen, formaldehyde least of all under the conditions used. However, the methane equilibrium, as well as methanol equilibrium, with carbon monoxide and hydrogen will be set up and in the presence of an excess of methane the whole system will shift toward methanol, a conception that may explain the survival of methanol independently of the time of contact. None of the catalysts are good catalysts for the methanol synthesis at high pressures, although copper is an excellent promoter of good catalysts. The alternative conception is that in the range of space velocities used insufficient time for decomposition of methanol was allowed. Both conceptions may play a part. The low yields found in experiments with the empty autoclave (Table 12) is explicable on the basis of both space velocity and Norrish's chain reaction. The space velocity was much smaller in these experiments and the time required for methanol decomposition may have been reached. The more likely explanation of the low yield however, is the predominance of reactions (2) and (3) above through the large gas phase in the empty autoclave with sub-

sequent decomposition of the aldehyde formed.

While the action of catalysts has been discussed in part, some further remarks regarding the effect of glass and enduro steel may be of value in the light of the above mechanism. The inaction of enduro steel may be attributed to its failure to absorb or combine with oxygen to any extent. This alloy, of the stainless type, is characterized by its resistance to oxidation. Consequently only the copper walls of the reactor would promote reaction(1), the reactions (2) and (3) taking place in the gas spaces between the enduro steel chips. There would be a consequent fall in yield as observed.

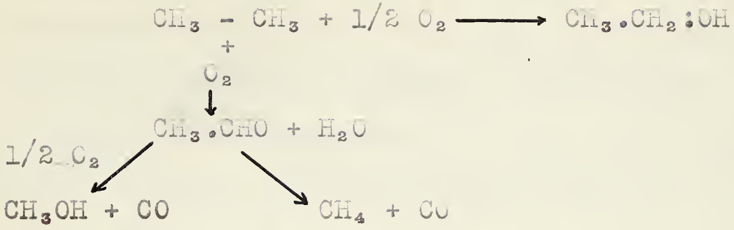
The reason for the efficiency of glass as a catalyst is not clear. One can suggest that it is a good catalyst for reaction (1) either through the adsorption of oxygen or methane, which is unlikely, or through some power of activation of the reactants. It is interesting to note that in the work of Bone and collaborators (3) on the oxidation of methane at atmospheric pressures, satisfactory surfaces such as porcelain, silica or glass were the most effective in promoting aldehyde formation. The assumption made by Bone was of course that methanol was the primary product. As an alternative, it may be suggested that the glass was not a catalyst at all but served the purpose of a deactivator of oxygen and broke the chains efficiently in Norrish,s reaction.

Consequently, the predominating reaction would be on the copper reactor surfaces to methanol.

The efficiency of silver may be attributed to the same property effective with copper, namely, its ability to absorb oxygen and its ease of oxidation and reduction. The observations of large amounts of formaldehyde with silver is not new and is somewhat inexplicable. The greater solubility of oxygen in silver with the possibility of a higher active concentration in the surface may account for the phenomenon. Methanol would be oxidized to formaldehyde or active oxygen may be liberated from the silver promoting reactions (2) and (3).

Returning to the experiments with natural gas, particularly those in Table 5, the behaviour of ethane is of interest. Sometimes all or nearly all of the ethane disappeared, the amount of methanol produced comparing with the ethane and frequently being greater. More interesting however are those experiments where the ethane in the off-gas was nearly the same as in the in-gas. Connected with the ethane is the reduction in temperature of the reaction, by 15-25°C., when using natural gas. ~~as compared to methane and showed a considerably lower ignition temperature even when present in small amounts~~. Moreover, it appeared to be able to cause oxidation of the methane at temperatures lower

than normal. The oxidation of ethane may be taken to follow the following mechanism:-



Between ethane and acetaldehyde, an intermediate stage analogous to the reaction (2) in Norrish's theory may intervene. The condensates from the natural gas experiments showed traces of ethyl alcohol by the iodoform test, confirming at least one reaction. No ethyl alcohol could be detected in the condensates from the methane experiments. The formation of acetaldehyde with its subsequent oxidation to methyl alcohol will explain the observed results that frequently the ethane burned could account for most of the methanol formed. The Oxidation of the methane at low temperatures may be accounted for by assuming the decomposition of acetaldehyde to produce activated molecules, the methane being able to react directly with the oxygen and the carbon monoxide to activate other methane molecules. Alternatively we may assume the formation of free radicles from the ethane as in Norrish's theory which are able to activate either methane or oxygen. Those experiments in which the ethane apparently survived are explicable

on the basis of free methylene groups formed according to reaction(2) of Norrish's theory. They will polymerize as in reaction (4) and may be hydrogenated with the formation of ethane. More probable is the formation of cyclo-propane a fairly stable hydrocarbon easily mistaken for ethane by the methods of gas analysis used. While all gas analysis combustions were in duplicate and checked, the small amounts of higher hydrocarbons above methane found could easily have been ethane or cyclo paraffins. The method of calculation, based on a small difference in large quantities, was such that ethane would not be distinguished from cyclopropane in the gas. The presence of higher cyclo-paraffins would interfere with the carbon monoxide and hydrogen determinations and may account for the difficulties of analysis found with some of the natural gas experiments.

There remain two observations for which no explanation can be offered at present. The reference is to the survival of the oxygen in all experiments and to the failure to obtain oxygen balances. The survival of traces of oxygen is real, many tests under various conditions showed it to be present in the off-gas, not as an accidental impurity but as a constituent leaving the reactor. The failure to obtain oxygen balances has been discussed, the present state of attempts to trace

the discrepancy suggests that the origin lies in the reactor and the catalyst.

Finally the bearing of the results on the utilization of natural gas may be discussed. The yields of methanol that may be obtained reach 75% under optimum conditions and some formaldehyde and formic acid are also produced. There is no reason to doubt that the yields can be raised still further. They are, however, high enough to warrant commercial investigation of the process as a source of methanol in competition with the water gas process. The process will have to be a circulatory one, present evidence showing that only low oxygen concentrations can be used in the production of high yields. Naturally pure oxygen will be required in place of air. Against these disadvantages may be set the two-stage nature of the water gas process and the more complicated high pressure apparatus.

Summary.

The effect of temperature, rate of off-gas flow and composition on the yields of the useful products in the oxidation of natural gas-air and methane-air mixtures has been investigated. The effect of pressure on the yield of the useful products was obtained in addition to the others for the methane-air mixtures.

A large percentage of oxygen in the natural gas or methane was found to be inimical to the survival of the useful oxidation products. At higher oxygen concentrations the yields fell off more rapidly in the methane-air mixtures than in the natural gas-air mixtures.

An optimum temperature of operation was obtained in the methane-air experiments. The optimum temperature of operation was found to decrease with an increase in the percentage of oxygen in the mixture. Increased pressures did not change the optimum temperature of operation to any great extent. Low temperatures of operation, preferably around 350 °C, are desirable in the oxidation of natural gas at 185 atmospheres pressure.

Pressures up to 184 atmospheres can be used advantageously at low oxygen concentrations to increase the survival of the useful products in the oxidation of methane. However, higher pressures are not desirable

since the yields of the useful products decrease. At high oxygen concentrations low pressures are more favorable for the survival of the primary oxidation product.

Space velocity in the range investigated is of little consequence in the oxidation of methane but is of some importance in the oxidation of natural gas.

Metallic catalysts of the active type as typified by silver and copper are efficient. Iron is detrimental to the reactions involved.

Methyl alcohol, the primary oxidation product, was obtained in yields as high as 74% of the methane oxidized, another 4% appearing as formaldehyde and formic acid. The liquid products contained up to 42.2% by weight of methyl alcohol. Lower yields were obtained with natural gas.

Bone's Hydroxylation theory does not offer a satisfactory explanation for the minor products of the reaction and the kinetics of the reaction. However, Norrish's theory explains many of these points. A mechanism combining aspects of both was presented to explain the observations made.

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